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Cu(I)-catalyzed stereospecific coupling reactions of enantioenriched α-stannylated benzyl carbamates and their application

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ABSTRACT

Enantioenriched α-stannylated benzyl carbamates were used in highly stereospecific coupling reactions employing Cu(I) as catalyzing transition metal. Acid chlorides and allyl bromide derivatives were used as electrophilic coupling partners. The reaction was applied in the synthesis of two highly enantioenriched indanoles and one enantioenriched tetraline via intramolecular cyclization reactions.

1. Introduction

Organostannanes are widely used in synthetic organic chemistry as valuable building blocks for the formation of carbon–carbon bonds via coupling reactions.[1] Besides the well established Stille reaction, where palladium is used as catalyzing transition metal,[2] copper-(co-)catalyzed Stille-type reactions emerged during the last years.[1,2] Although used as catalyst or promoter itself in numerous applications,[3] copper was found to be a versatile co-catalyst in Stille-type reactions as firstly systematically demonstrated by Liebeskind and co-workers.[4–7] Nowadays, various examples exist in which copper is used as the only catalytic or promoting transition metal;[1,4c,7–11] thereby, a broad variety of substrates has been employed, utilizing both sp^2- and sp^3-hybridized tin moieties bearing carbon centers (Fig. 1). Very often, these carbons are additionally attached to functional groups via different heteroatoms.

During their studies in this field of transition metal catalyzed coupling reactions, Falck and co-workers also have reported on stereospecific copper(I)-catalyzed coupling reactions of various stannanes, among them α-oxygenated benzylstannanes **4**.[12] However, no statements have been made concerning the stereospecific copper(I)-catalyzed coupling reaction of highly enantioenriched, *O*-protected α-stannylated benzyl alcohols. As we have developed a reliable asymmetric method for synthesizing highly enantioenriched α-stannylated benzyl carbamates **6** and **7** in high yields,[13] and as we had noticed highly stereospecific coupling reactions of allylic stannanes,[14] we became interested in the use of the α-stannylated benzyl carbamates in stereospecific coupling reactions.[15] Herein we report on both our results concerning copper(I)-catalyzed coupling reactions of different benzyl-type stannanes with allyl bromide derivatives and acid chlorides and the application of the procedure in synthetic problems.

2. Catalyst screening and discussion of the stereochemistry

Choosing the coupling of α-stannylated benzyl carbamate **6** with allyl bromide in toluene[16] as the reaction for catalyst screening, we obtained the results outlined in Table 1.[17] Independent of the

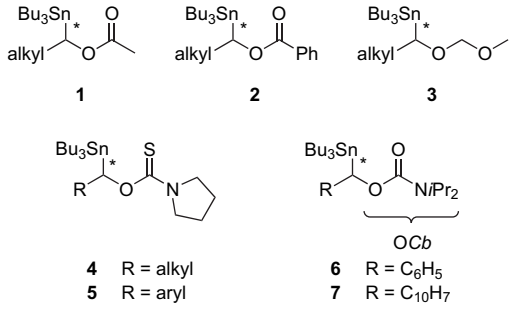

Figure 1. Different organostannanes already used in copper-catalyzed coupling reactions (**1**–**5**) and α-stannylated benzyl carbamates **6** and **7**.

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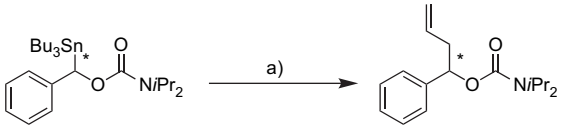
Table 1
Results of catalyst screening

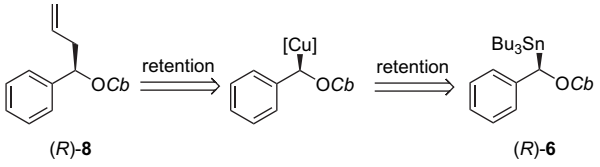


Entry	Stannane **6** (*R*/*S*) (% ee)	Cu(I)X (mol %)	*t* (coupling) (h)	Yield (%)	$[\alpha]_D^{20}$ (*c*, $CHCl_3$)	% ee	Configuration of product **8**	Stereospecificity *S* (%)
1[a]	(*R*)-**6** (80)	CuCN (10)	24	87	+3.0 (1.07)	75	*R*	94
2[b]	(*S*)-**6** (93)	CuCN (10)	48	74	−3.3 (1.56)	90	*S*	97
3[a]	(*R*)-**6** (80)	CuI (10)	40	59	—	76	*R*	95
4[c]	(*S*)-**6** (99)	CuCN·2LiCl (10)	36	74	—	95	*S*	96
5[c]	(*S*)-**6** (99)	CuTC[d] (10)	36	74	−3.7 (1.02)	96	*S*	97

Reaction conditions: (a) cat. Cu(I)X, allyl bromide, toluene, 70 °C, *t* (coupling).
[a] Stannane (*R*)-**6** was synthesized using (−)-sparteine as chiral ligand; see Ref. 13c for details.
[b] Stannane (*S*)-**6** was synthesized using bis(oxazoline) ligand **27** as described in Refs. 13a,b; epimeric complexes not fully equilibrated when being trapped with tributyltin chloride.
[c] Stannane (*S*)-**6** was synthesized using bis(oxazoline) ligand **27** as described in Refs. 13a,b.
[d] CuTC: copper(I) thiophene-2-carboxylate.[17]

copper(I)-salt employed and the enantioenrichment of the stannane used, all reactions took place with the same stereospecificity *S* of about 95%. Since the counter ion seems to have no influence on the stereochemistry, all the copper(I) sources can be used in fact. The results further show that the intermediate copper species must be configurationally stable. We assume that the carbamate group plays an important role here, as it can coordinate to the copper by its carbonyl oxygen atom.[18] The best yield (87%) and the best stereospecificity was obtained when the reaction was catalyzed by CuCN under 'sealed tube' conditions (Table 1, entries 2 and 3). 10 mol % of copper(I) salt turned out to be the minimum catalyst loading; lower loadings resulted in poorer conversion and yields.

The absolute configurations of both the substrate and the product—determined via comparison of their optical rotations with literature values[13]—reveal that the reactions took place with net retention of configuration (Scheme 1). The entire reaction can be separated into one transmetallation step and one substitution step. It is known that the tin–copper transmetallation proceeds under retention of configuration;[19] therefore the substitution step must be retentive as well. These findings fit in the current knowledge concerning this kind of reactions[19a,g,20,21] and are underlined by further experiments (vide infra).

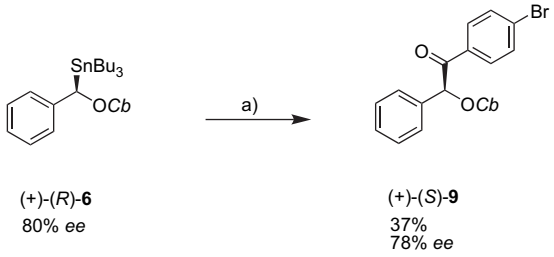


Scheme 1. Stereochemical aspects of the coupling reaction outlined in Table 1.

The amount of observed stereospecificity *S* as well as the net retention of configuration for the complete reaction was confirmed when *para*-bromobenzoyl chloride was used as electrophilic coupling partner (Scheme 2). Starting from stannane (*R*)-**6** (er=90:10), ketone (*S*)-**9**, formed in 37% yield, exhibited an enantiomeric ratio of 89:11 in favor of the *S*-configured enantiomer as it could be determined from both the comparison of optical rotation with the literature values[13] and an X-ray crystal structure analysis under anomalous dispersion (Fig. 2).

3. Scope and limitations

We then used different allyl bromides and acid chlorides as electrophilic coupling partners under the reaction conditions



Scheme 2. Coupling of stannane **6** with *para*-bromobenzoyl chloride. Reaction conditions: (a) 10 mol % CuCN, 4-Br-$C_6H_4C(=O)Cl$, toluene, 70 °C, 36 h.

outlined in Scheme 1 to scope the reaction. The results are listed in Table 2. Employing *trans*-crotyl bromide as electrophilic coupling partner resulted in an inseparable complex mixture of linear S_N2 coupling by-product and branched S_N2' coupling products **10** as diastereomeric mixture with a slight preference for the trans-isomer (Table 2, entry 1).[23] Formation of diastereomers here arises from a non stereodifferentiating attack at the double bond. It was not possible to determine the enantiomeric ratios of the products; the overall yield was satisfying. Coupling of *trans*-bromo-crotonic acid methyl ester[24] yielded desired ester **12** as an inseparable *syn*/*anti*-mixture in 64% overall yield (Table 2, entry 2). The enantiomeric excess was determined from the mixture of diastereomers to be greater than 90% ee, corresponding to a stereospecificity *S* greater than 93% for this coupling partner. Noteworthy, we did not find a linear coupling product emerging from a S_N2 type reaction in this case.

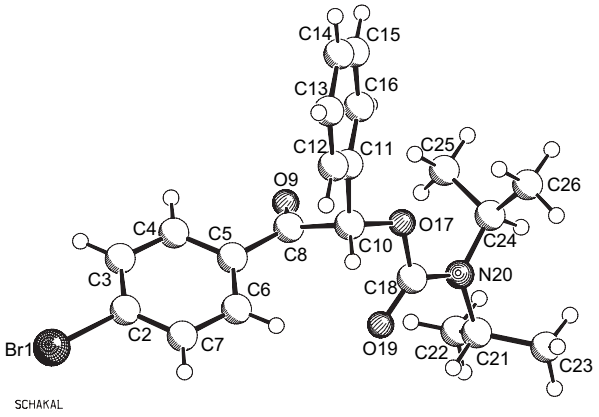
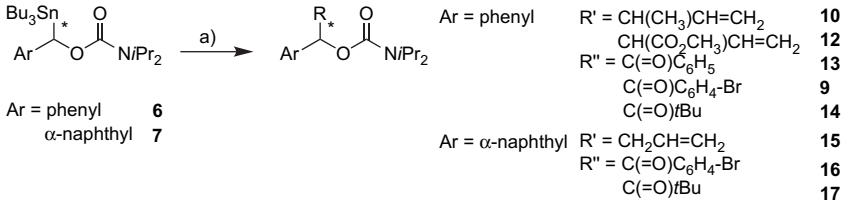
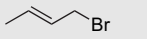
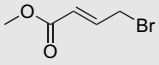
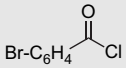
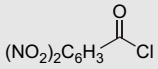
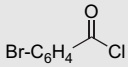


Figure 2. X-ray crystal structure of ketone (+)-(*S*)-**9**.[22]

Table 2
Results of further coupling experiments employing benzylstannanes



Entry	Stannane (*R*/*S*) (% ee)	Coupling partner	*t* (coupling) (h)	Yield (%)	dr	$[\alpha]_D^{20}$ (*c*, $CHCl_3$)	% ee[a]	Product/ configuration	Stereospecificity *S* (%)
1	(*S*)-**6** (97)[b]		16	66[c]	1.4:1	—	n.d.[d]	*syn*-**10**/*S*,*R*; *anti*-**10**/*S*,*S*	n.d.
2	(*S*)-**6** (97)[b]		48	64	1.1:1	—	*syn*/>90;[e] *anti*/>90[e]	*syn*-**12**/*S*,*R*; *anti*-**12**/*S*,*S*	*syn*/>93; *anti*/>93
3	(*R*)-**6** (31)[f]		36	48	—	+59.5 (0.89)	30	**13**/*S*	95
4	(*S*)-**6** (98)[b]		48	54	—	−183.6 (0.98)	92	**13**/*R*	94
5	(*R*)-**6** (80)[g]		36	37	—	+79.5 (1.25)	78	**9**/*S*	97
6	(*S*)-**6** (98)[b]		48	50	—	−120.2 (1.01)	94	**9**/*R*	96
7	(*R*)-**6** (80)[g]		36	—	—	—	—	—	—
8	(*S*)-**6** (98)[b]		36	37	—	−200.2 (0.66)	93	**14**/*R*	95
9	(*S*)-**7** (99)[h]		16	80	—	+26.3 (0.96)	95% op	**15**/*S*	96
10	(*S*)-**7** (99)[h]		18	66	—	−277.8 (0.74)	97	**16**/*R*	98
11	(*S*)-**7** (99)[h]		36	44	—	+58.6 (0.22)	n.d.	**17**/*R*	n.d.

Reaction conditions: (a) 10 mol% CuCN, coupling partner, toluene, 70 °C, *t* (coupling).
[a] Determined by HPLC on chiral stationary phase; see Section 6 for details.
[b] Stannane (*S*)-**6** was synthesized using bis(oxazoline) ligand **27**; see Refs. 13a,b.
[c] Product contains the linear S_N2-reaction product ((*E*)-*N*,*N*-diisopropylcarbamic acid 1-phenyl-pent-3-enyl ester) as by-product.
[d] Due to the linear side product, the determination of the enantiomeric excess was not possible.
[e] Determined out of the mixture of diastereomers. The signal of the second enantiomers was not detectable.
[f] Stannane (*R*)-**6** was synthesized using (−)-sparteine; see Refs. 13a,b.
[g] Stannane (*R*)-**6** was synthesized using (−)-sparteine; see Ref. 13c.
[h] Stannane (*S*)-**7** was synthesized using bis(oxazoline) ligand; see Refs. 13a,b.

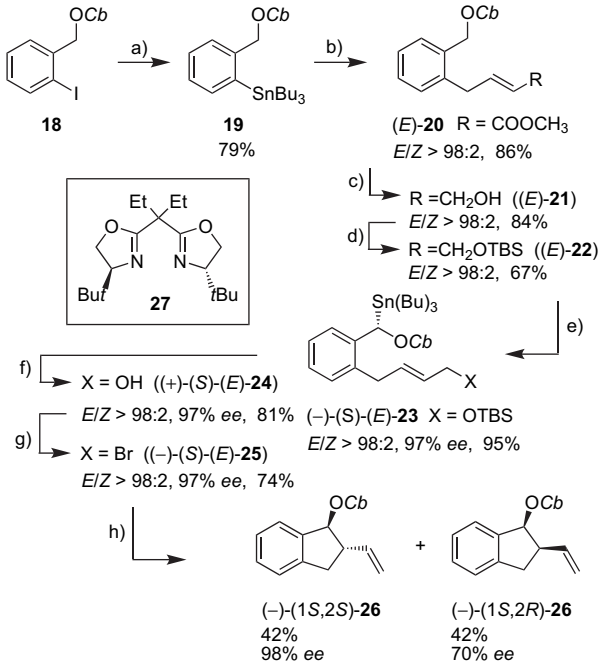
The experiments shown in entries 4–8 in Table 2 underline the result presented in Scheme 2 and discussed above. Unsubstituted benzoyl chloride reacts in moderate yields up to 56% with the expected stereospecificity. Extension of the reaction time improved the yield of **9** in the coupling of *para*-bromobenzoyl chloride up to 50% (Table 2, entry 6; for entry 5, compare Scheme 2) without change in stereospecificity. 2,4-Dinitrobenzoyl chloride did not react under these conditions (Table 2, entry 7), thereby revealing that electron-poor coupling partners are problematic. Aliphatic pivaloyl chloride can be used as well (Table 2, entry 8). Albeit formed in comparably moderate 37% yield, the enantioenrichment of aliphatic ketone **14** (93% ee) shows 95% retention of configuration.

Employing highly enantioenriched α-stannylated 1-naphth-1-ylmethyl carbamate **7** delivered similar results (Table 2, entries 9–11). Couplings employing allyl bromide and different acid chlorides proceeded in good yields with very high stereospecificity *S*.

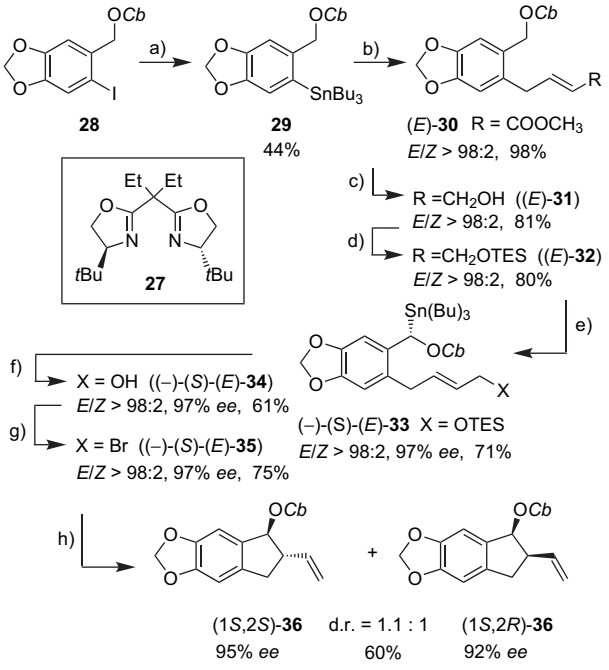
4. Intramolecular cyclization reactions

We then used the reaction presented above in intramolecular cyclization reactions in order to gain access to indanoles and similar structures.[25] The cyclization precursor **25** was synthesized straightforward as it is displayed in Scheme 3.

ortho-Iodo-benzyl carbamate **18** was transformed into stannane **19** according to protocols developed by Knochel and co-workers.[26] Stannane **19** was then coupled to *trans*-bromo-crotonic acid methyl ester under standard Stille-type conditions to form the carbon skeleton of the cyclization precursor (*E*)-**20**. Further standard



Scheme 3. Synthesis of indanoles **26**. Reaction conditions: (a) (i) ^{i}PrMgCl, THF, −40 °C; 2 h; (ii) Bu_3SnCl, THF, −40 °C→rt, 4 h; (b) 10 mol % $Pd_2(dba)_3$, (*E*)-4-bromo-crotonic acid methyl ester, DMF, 60 °C, 60 h; (c) DIBAL-H, THF, −78 °C, 1 h; (d) NEt_3, cat. DMAP, TBSCl, THF, rt, 12 h; (e) (i) bis(oxazoline) **27**, ^{s}BuLi, Et_2O, −78 °C, 2.5 h; (ii) Bu_3SnCl, −78 °C, 3 h; (iii) MeOH, H_2O; (f) TBAF, THF/Et_2O=3:2, 0 °C, 12 h (TLC control); (g) PPh_3, CBr_4, CH_2Cl_2, rt, 1 h; (h) CuCN (20 mol %), toluene, 70 °C, 72 h.



Scheme 4. Synthesis of indanoles **36**. Reaction conditions: (a) (i) ^{n}BuMgCl, ^{n}BuLi, THF, −78 °C, 2 h; (ii) Bu_3SnCl, THF, −78 °C→rt, 4 h; (b) 10 mol % $Pd_2(dba)_3$, (*E*)-4-bromo-crotonic acid methyl ester, DMF, 70 °C, 36 h; (c) DIBAL-H, THF, −78 °C, 1 h; (d) NEt_3, cat. DMAP, TESCl, THF, rt, 12 h; (e) (i) bis(oxazoline) **27**, ^{s}BuLi, Et_2O, −78 °C, 2.5 h; (ii) Bu_3SnCl, −78 °C, 3 h; (iii) MeOH, H_2O; (f) TFA, THF/H_2O=1:1, 0 °C, TLC control; (g) PPh_3, CBr_4, CH_2Cl_2, rt, 1 h; (h) CuCN (15 mol %), toluene, 70 °C, 72 h.

transformations delivered primary benzyl carbamate (*E*)-**22**. Asymmetric stannylation employing bisoxazoline (−)-(*S*,*S*)-**27**[27] for induction of chiral information yielded α-stannylated benzyl carbamate (−)-(*S*)-(*E*)-**23** in 95% yield. Desilylation afforded allyl alcohol (−)-(*S*)-(*E*)-**24**.[28] On this stage, the enantiomeric excess was determined to be 97% ee. An Appel reaction finally afforded cyclization precursor (−)-(*S*)-(*E*)-**25**.[29] The double bond geometry remained untouched during the transformations.

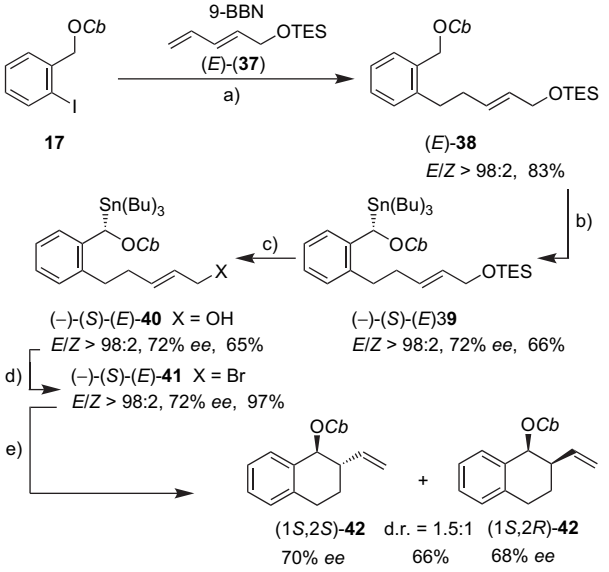
Intramolecular coupling of stannane **25** was achieved employing 15 mol % CuCN (Scheme 3), and the desired *O*-carbamoylated indanole was obtained as a 1:1-mixture of the trans- and the cis-product, which could be separated by simple flash chromatography.[30] Whereas *trans*-**26** was formed with high stereospecificity (98% ee), the cis-isomer *cis*-**26** was only formed with 72% retention of configuration here. The reasons remain unknown so far.

Concerning mechanistical aspects we assume that the initial tin–copper transmetallation is followed by a complexation of the intermediate copper species by the olefin. Within this complex the C–C bond formation takes place, finally forming vinylic double bond in indanoles **26**.

The absolute configuration of the cyclization products was rationalized as follows. We have shown earlier that the bis(oxazoline) **27** containing epimeric lithium complexes formed of primary benzyl carbamates equilibrate and that the (R_C)-configured epimer is strongly favored under the reactions conditions, which were employed here as well.[13] We have further shown that these facts are not influenced by *ortho*-substituents on the aryl moiety.[13c] Trapping of the equilibrated lithium species with tributyltin chloride proceeds under inversion of configuration, delivering (*S*)-configured stannanes. Stereospecific coupling as outlined above therefore yields the (1*S*)-configured cyclic products *trans*- and *cis*-**26** here.

Comparable results were obtained when cyclization of precursor (−)-(*S*)-(*E*)-**35** was performed by using this coupling procedure (Scheme 4). Highly enantioenriched precursor (−)-(*S*)-(*E*)-**35** was derived from carbamoylated benzyl alcohol **28**[31,32] by standard transformations[33] including an asymmetric stannylation in order to form the benzylic stereogenic center. Again, the copper catalyzed coupling reaction proceeded stereospecifically (*S*=95–98%), resulting in an inseparable 1:1-mixture (60% yield) of highly enantioenriched indanole derivatives *trans*-**36** (95% ee) and *cis*-**36** (92% ee).[34] Here again, the formation of the cis-isomer suffers from a somewhat lower stereospecificity.

Tetraline systems can be obtained via this procedure as well as it is outlined in Scheme 5. The synthesis of the enantioenriched cyclization precursor (−)-(*S*)-(*E*)-**41** started with a *B*-alkyl Suzuki–



Scheme 5. Synthesis of tetralines **42**. Reaction conditions: (a) (i) 9-BBN, (*E*)-**37**; (ii) K_3PO_4, 3 mol % $Pd(PPh_3)_4$, DMF, 60 °C, 32 h; (b) (i) bis(oxazoline) ligand **27**, ^{s}BuLi, Et_2O, −78 °C, 2.5 h; (ii) Bu_3SnCl, −78 °C, 3 h; (iii) MeOH, H_2O; (c) TFA, THF/H_2O=1:1, 0 °C, TLC control; (d) PPh_3, CBr_4, CH_2Cl_2, rt, 1 h; (e) CuCN (15 mol %), toluene, 70 °C, 72 h.

Miyaura coupling reaction[35] in order to attach the unsaturated side chain to benzyl carbamate **17**. This reaction was followed by an asymmetric stannylation according to the standard protocol[13] yielding stannane **39** in moderate yield (66%) and with comparably low enantioselectivity of 72% ee, which again was measured at the stage of allyl alcohol derivative (−)-(*S*)-(*E*)-**40**. The more flexible side chain is blamed to disturb the asymmetric stannylation here. After formation of allyl bromide **41**, the stereospecific coupling procedure (94–97% retention of configuration) yielded diastereomeric tetralines *trans*-**42** (70% ee) und *cis*-**42** (68% ee)[34] in 66% yield as an inseparable mixture with the *anti*-isomer slightly preferred (*trans*/*cis*=1.5:1).

5. Conclusion

We have shown that enantioenriched α-stannylated benzyl carbamates can be coupled with allyl bromides and acid chlorides using CuCN as catalyst. The coupling reactions proceed with high stereospecificity. The procedure was applied in the syntheses of enantioenriched indanoles and an enantioenriched tetraline.

6. Experimental

6.1. General

All solvents were dried and purified prior to use. Toluene was distilled over sodium/benzophenone. TESCl was distilled from powdered CaH_2 and stored under argon. *sec*-Butyllithium as solution in hexane/cyclohexane=92:8 was filtered through Celite before use and its concentration was determined by titration against diphenylacetic acid.[36] E refers to: Et_2O, H: *n*-hexane, P: pentane, TBME: *tert*-butyl methyl ether, DMF: dimethylformamide. All air and moisture sensitive reactions were performed under argon atmosphere in flame-dried glassware using septum and syringe techniques. Flash column chromatography (FCC) was performed on Merck 60 silica gel, 0.040–0.063 mm, using an argon pressure of 1.2–1.4 bar, and monitored by thin-layer chromatography (TLC) on Merck 60 F_{254} silica gel. Gas chromatography was performed on Agilent 6890 plus, Agilent, Böblingen. HP 5, HP 1701 were used as achiral columns (HP 5: 30 m long, 0.32 μm diameter, 0.25 mm thick stationary phase, N_2 as the mobile phase, 106 kPa pressure, 290 °C injection temperature, 300 °C detector temperature, program: 50 °C start temperature, 10 °C min^{-1} heating rate, 300 °C final temperature for 15 min) (HP 1701: 25 m long, 0.20 μm diameter, 0.20 mm thick stationary phase, N_2 as the mobile phase, 100 kPa pressure, 250 °C injection temperature, 300 °C detector temperature, program: 50 °C start temperature, 10 °C min^{-1} heating rate, 270 °C final temperature for 20 min). Melting points were measured on an SMP3 melting point apparatus purchased from Stuart Scientific, UK (uncorrected values). The optical rotations were measured in a 10 cm cuvette on a polarimeter 341 purchased from Perkin–Elmer. Unless otherwise stated, ^1H and ^{13}C NMR data were recorded on Bruker ARX 300 and AMX 400; spectra were obtained from solutions in $CDCl_3$ (δ_C=77.0 ppm) and were calibrated relative to residual content of $CHCl_3$ (δ_H=7.24 ppm) or $SiMe_4$ (δ_H=0.0 ppm). Peak multiplicities in ^1H NMR spectra are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), br (broad), and ps (pseudo). Diastereotopic methylene protons with different chemical shifts are abbreviated as H_A and H_B. IR: Nicolet 5DCX, Bruker IFS 28 or Varian 3100 Excalibur Series with Specac Golden Gate Single Reflection ATR. Elemental analyses were performed at the Microanalytical Section of the Organisch-Chemisches Institut, WWU Münster, on a Vario El III, purchased from Elementar Analysen Systeme, Hanau (Germany). Mass spectrometric data were obtained on Finnigan MAT 8230 (EI), Micromass Quattro LCZ (ESI), Micromass MAT 8200 (GC-TOF/HRMS). HPLC: Waters 600E Multisolvent Delivery System and 996 PDA detector. Crystallographic data: data set was collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[37] absorption correction Denzo,[38] structure solution SHELXS-97,[39,40] structure refinement SHELXL-97,[41] graphics SCHAKAL.[42] *N*,*N*-Dimethylamino pyridine (DMAP), palladium tetrakis(triphenylphosphine) ($Pd(PPh_3)_4$), and palladium dibenzylidene-acetone ($Pd_2(dba)_3$) were used as purchased. Electrophilic coupling partners were purified before use (exception: solids). Literature known compounds are not fully characterized again. Bis(oxazoline) ligand **27** was prepared according to the literature.[27] Stannanes **6** and **7** were prepared as described earlier.[13] Spectroscopic data of coupling products **8**, **9**, **14**, and **15** correspond to the literature.[13]

6.2. Typical procedure for the synthesis of coupling products 8–10, 12–17 (GPA)

CuCN (dried) of 10 mol % was filled in a flame-dried Schlenk tube, which is evacuated and flooded again with argon. Dry toluene of 5.0 mL was then added. Electrophilic coupling partner (0.36 mmol, 1.2 equiv) and 0.30 mmol (1.0 equiv) of benzyl stannane were injected into this suspension. The reaction mixture was stirred at 70 °C for the given time (see Tables 1 and 2) under sealed tube conditions until complete conversion of the stannane (TLC). The reaction mixture is cooled down to rt and diluted with 10 mL of TBME. Satd ammonia of 2 mL was added and the phases were separated. The aqueous phase was extracted with TBME (3×10 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude products were purified by flash chromatography on silica gel with *E*/*P*-mixtures.

*6.2.1. (−)-(S)-N,N-Diisopropylcarbamic acid (1-phenyl-but-3-enyl) ester (**8**)*

According to GPA, stannane **6** (93% ee, 158 mg, 0.30 mmol) was reacted with allyl bromide (44 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **8** (72 mg, 87%) as colorless oil. R_f 0.65 (*E*/*P*=1:1); t_R 14.4 min (HP 5); $[\alpha]_D^{20}$ −3.3 (*c* 1.56, $CHCl_3$); HPLC: CHIRA-GROM 2 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(−) 9.1 min, t_R(+) 11.5 min, 90% ee.

*6.2.2. (+)-(S)-N,N-Diisopropylcarbamic acid [2-(4-bromo-phenyl)-2-oxo-1-phenyl-ethyl] ester (**9**)*

According to GPA, stannane **6** (80% ee, 158 mg, 0.30 mmol) was reacted with 4-bromobenzoyl chloride (79 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **9** (46 mg, 37%) as colorless solid. R_f 0.34 (*E*/*P*=1:2); t_R 21.4 min (HP 5); $[\alpha]_D^{20}$ +79.5 (*c* 1.25, $CHCl_3$); HPLC: CHIRA-GROM 2 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(−) 58.0 min, t_R(+) 79.1 min, 78% ee.

*6.2.3. N,N-Diisopropylcarbamic acid (2-methyl-1-phenyl-but-3-enyl) ester (**10**)*

According to GPA, stannane **6** (97% ee, 158 mg, 0.30 mmol) was reacted with *trans*-crotyl bromide (49 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **10** as an inseparable 1.4:1-mixture of diastereomers (GC), additionally containing traces of linear coupling product, as colorless liquid (57 mg). Data for *syn*-**8** and *anti*-**8**: R_f 0.67 (*E*/*P*=1:1); t_R 11.6 min (1*R*,2*S**), 12.2 min (1*R*,2*R**) (HP 5); ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (d, ^3J=6.9 Hz, 3H, –CH_3 (1*R*,2*S**)), 0.97 (d, ^3J=6.9 Hz, 3H, –CH_3 (1*R*,2*R**)), 1.14 (ps-s, 24H, (H_3C)$_2$CH– (1*R*,2*S*) and (1*R*,2*R*)), 2.48 (m, 1H, *CH*CH$_3$ (1*R*,2*S**)), 2.63 (m, 1H, *CH*CH$_3$ (1*R*,2*R**)), 3.88 (ps-s, 4H, (H_3C)$_2$*CH*– (1*R*,2*S*) and (1*R*,2*R*)), 4.93 (m, 4H, H_2CCH– (1*R*,2*S*) and (1*R*,2*R*)), 5.60 (m, 4H, $H_{benzylic}$, H_2C*CH*– (1*R*,2*S*) and (1*R*,2*R*)), 7.13–7.32 (m, 10H, H-ph, (1*R*,2*S*) and (1*R*,2*R*)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4 (*C*H$_3$ (1*R*,2*S**)), 16.5 (CH$_3$ (1*R*,2*R**)), 21.1 ((H_3C)$_2$CH– (1*R*,2*S*) and (1*R*,2*R*)),

40.2 (H_2CCH– (1*R*,2*S**)), 43.2 (H_2CCH– (1*R*,2*R**)), 45.8 (($H_3C)_2CH$– (1*R*,2*S*) and (1*R*,2*R*)), 79.6 ($C_{benzylic}$ (1*R*,2*S**)), 79.8 ($C_{benzylic}$ (1*R*,2*R**)), 115.3 (H_2CCH– (1*R*,2*S*) and (1*R*,2*R*)), 125.2, 126.4, 127.1, 127.3, 127.9, 128.0 (C-ph without C-2 (1*R*,2*S*) and (1*R*,2*R*)), 139.7 (C_{ipso} (1*R*,2*S**)), 140.2 (C_{ipso} (1*R*,2*R**)), 154.8 (NC═O (1*R*,2*S**)), 155.0 (NC═O (1*R*,2*R**)); IR (ATR) 3065, 3033, 2970, 2935, 2876, 1695, 1653, 1541, 1475, 1457, 1436 cm^{-1}; MS (ESI) *m*/*z* 312.1934 $[M+Na]^+$. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.35; H, 9.47; N, 4.74.

6.2.4. 2-(N,N-Diisopropylcarbamoyloxy-2-phenyl-methyl)-but-3-enoic acid methyl ester (**12**)

According to GPA, stannane **6** (97% ee, 158 mg, 0.30 mmol) was reacted with *trans*-4-bromo-crotonic acid methyl ester (158 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **12** as an inseparable 1.1:1-mixture of diastereomers (GC) as colorless liquid (52 mg, 52%). Data for *syn*-**12** and *anti*-**12**: R_f 0.49 (*E*/*P*=1:1); t_R 13.5 min (1*R*,2*R*) and (1*R*,2*S*) (HP 5); $[\alpha]_D^{20}$ −5.6 (*c* 0.75, $CHCl_3$); HPLC: CHIRA-GROM 2 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(1*S*,2*S**) 15.4 min, t_R(1*R*,2*S**) 16.9 min, >90% ee; t_R(1*S*,2*R**) 18.3 min, t_R(1*R*,2*R**) 22.3 min, >90% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (ps-s, 24H, ($H_3C)_2CH$– (1*R*,2*S*) and (1*R*,2*R*)), 3.50 (dd, ^3J=7.6, 9.3 Hz, 1H, –C*H*– (1*R*,2*S*)), 3.51 (s, 3H, –OCH_3 (1*R*,2*R*)), 3.58 (dd, ^3J=^3J=9.4 Hz, 1H, –C*H*– (1*R*,2*R*)), 3.66 (s, 3H, –OCH_3 (1*R*,2*S*)), 3.87 (ps-s, 4H, ($H_3C)_2CH$– (1*R*,2*R*) and (1*R*,2*S*)), 4.90–5.20 (m, 4H, H_2C═CH– (1*R*,2*R*) and (1*R*,2*S*)), 5.58 (ddd, ^3J=17.2, 8.9, 9.4 Hz, 1H, H_2C═C*H*– (1*R*,2*R*)), 5.92 (d, ^3J=9.4 Hz, 1H, $H_{benzylic}$ (1*R*,2*R*)), 5.93 (ddd, ^3J=17.2, 9.3, 9.3 Hz, 1H, H_2C═C*H*– (1*R*,2*S*)), 6.09 (d, ^3J=9.3 Hz, 1H, $H_{benzylic}$ (1*R*,2*S*)), 7.08–7.35 (m, 10H, H-ph (1*R*,2*R*) and (1*R*,2*S*)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 (($H_3C)_2CH$– (1*R*,2*R*) and (1*R*,2*S*)), 45.9 (($H_3C)_2CH$– (1*R*,2*R*) and (1*R*,2*S*)), 51.8 (–*C*H– (1*R*,2*R**)), 51.9 (–*C*H– (1*R*,2*S**)), 56.7 (–OCH_3 (1*R*,2*R**)), 57.5 (–OCH_3 (1*R*,2*S**)), 76.0 ($C_{benzylic}$ (1*R*,2*R**)), 76.7 ($C_{benzylic}$ (1*R*,2*S**)), 119.9 (H_2C═CH– (1*R*,2*S**)), 120.1 (H_2C═CH– (1*R*,2*R**)), 126.9, 127.4, 127.9, 128.0, 128.2, 128.2 (C-ph without C_{ipso} (1*R*,2*S*) and (1*R*,2*R*)), 131.3 (H_2C═*C*H– (1*R*,2*R**)), 132.5 (H_2C═*C*H– (1*R*,2*S**)), 138.4 (C_{ipso} (1*R*,2*S**)), 138.8 (C_{ipso} (1*R*,2*R**)), 154.0 (NC═O (1*R*,2*R**)), 154.2 (NC═O (1*R*,2*S**)), 171.1 (*C*═O (1*R*,2*R**)), 171.7 (*C*═O (1*R*,2*S**)); IR (ATR) 3061, 3026, 2969, 2878, 1720, 1693, 1650, 1585, 1549, 1495, 1433 cm^{-1}; MS (ESI) *m*/*z* 356.1834 $[M+Na]^+$. Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20. Found: C, 68.18; H, 8.28; N, 4.18.

6.2.5. (+)-(S)-N,N-Diisopropylcarbamic acid 2-oxo-1,2-diphenyl-ethyl ester (**13**)

According to GPA, stannane **6** (31% ee, 158 mg, 0.30 mmol) was reacted with benzoyl chloride (51 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **13** (49 mg, 48%) as colorless solid. R_f 0.53 (*E*/*P*=1:1); t_R 18.7 min (HP 5); mp 129 °C (E); $[\alpha]_D^{20}$ +59.5 (*c* 0.89, $CHCl_3$); HPLC: CHIRA-GROM 1 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(−) 53.9 min, t_R(+) 68.2 min, 30% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, ^3J=6.8 Hz, 12H, ($H_3C)_2CH$–), 3.87 (ps-s, 1H, ($H_3C)_2CH_B$), 4.04 (ps-s, 1H, ($H_3C)_2CH_A$–), 6.88 (s, 1H, $H_{benzylic}$), 7.26–7.42 (m, 5H, H_{ortho}, H_{meta}, H_{para}), 7.44–7.53 (m, 3H, $H_{meta'}$, $H_{para'}$), 7.95 (dd, ^3J=8.7 Hz, ^4J=1.6 Hz, 2H, $H_{ortho'}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6 (($H_3C)_2CH$–), 46.2 (($H_3C)_2CH$–), 77.4 ($C_{benzylic}$), 128.5, 128.6, 128.7, 128.8, 128.9, 133.1, 134.4, 135.1 (C-ph), 154.7 (N*C*═O), 195.2 (*C*═O); IR (KBr): 3065, 3007, 2974, 2931, 2872, 1677, 1596, 1475, 1446, 1440, 1384, 1368 cm^{-1}; MS (ESI) *m*/*z* 362.1737 $[M+Na]^+$. Anal. Calcd for $C_{21}H_{25}NO_3$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.10; H, 7.40; N, 3.98.

6.2.6. (−)-(R)-N,N-Diisopropylcarbamic acid (3,3-di-methyl-2-oxo-1-phenyl-butyl) ester (**14**)

According to GPA, stannane **6** (98% ee, 158 mg, 0.30 mmol) was reacted with pivaloyl chloride (43 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **14** (35 mg, 37%) as colorless liquid. R_f 0.37 (*E*/*P*=1:3); t_R 14.5 min (HP 5); $[\alpha]_D^{20}$ −200.2 (*c* 0.66, $CHCl_3$); HPLC: CHIRA-GROM 2 (2×250 mm), H/^{i}PrOH=1000:1, 0.2 mL min^{-1}, λ 210 nm, t_R(+) 11.6 min, t_R(−) 12.8 min, 93% ee.

6.2.7. (+)-(S)-N,N-Diisopropylcarbamic acid 1-(naphth-1-yl-but-3-enyl) ester (**15**)

According to GPA, stannane **7** (99% ee, 172 mg, 0.30 mmol) was reacted with allyl bromide (44 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **15** (78 mg, 80%) as colorless oil. R_f 0.64 (*E*/*P*=1:1); t_R 17.5 min (HP 5); $[\alpha]_D^{20}$ +26.3 (*c* 0.96, $CHCl_3$), 95% op.

6.2.8. (−)-(R)-N,N-Diisopropylcarbamic acid [2-(4-bromo-phenyl)-1-(naphth-1-yl)-2-oxo-ethyl] ester (**16**)

According to GPA, stannane **7** (99% ee, 172 mg, 0.30 mmol) was reacted with 4-bromo-benzoyl chloride (79 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **16** (106 mg, 75%) as colorless highly viscous oil. R_f 0.69 (*E*/*P*=1:1); t_R 21.2 min (HP 5); $[\alpha]_D^{20}$ −277.1 (*c* 1.01, $CHCl_3$); HPLC: CHIRA-GROM 2 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ=210 nm, t_R(+) 29.3 min, t_R(−) 35.1 min, 97% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (br d, ^3J=7.0 Hz, 6H, ($H_3C)_2CH$–), 1.89 (d, ^3J=6.9 Hz, 6H, ($H_3C)_2CH$–), 3.76 (ps-s, 1H, ($H_3C)_2CH$–), 3.98 (ps-s, 1H, ($H_3C)_2CH$–), 7.03–7.59 (m, 8H, $H_{benzylic}$, H-2, H-3, H-7, H-ph), 7.67 (d, ^3J=8.6 Hz, 1H, H-6), 7.80 (br dd, ^3J=^3J=8.8 Hz, 2H, H-4, H-5,), 8.23 (d, ^3J=8.4 Hz, 1H, H-9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2 (($H_3C)_2CH$–), 46.4 (($H_3C)_2CH$–), 74.9 ($C_{benzlic}$), 123.5, 125.3, 125.4, 126.2, 127.1, 128.2, 128.3, 128.9, 129.0, 130.0, 130.1, 130.3, 131.4, 131.8, 133.8, 134.2, 137.9 (C-naph, C-ph), 154.5 (NC═O), 194.9 (C═O); IR (KBr) 3086, 3062, 3052, 2970, 2933, 2875, 1682, 1586, 1568, 1512, 1476, 1435 cm^{-1}; MS (ESI) *m*/*z* 468.1165 $[M+H]^+$. Anal. Calcd for $C_{25}H_{26}BrNO_3$: C, 64.11; H, 5.60; N, 2.99. Found: C, 64.38; H, 5.50; N, 2.95.

6.2.9. (+)-(R)-N,N-Diisopropylcarbamic acid (3,3-di-methyl-1-(naphth-1-yl)-2-oxo-butyl) ester (**17**)

According to GPA, stannane **7** (99% ee, 172 mg, 0.30 mmol) was reacted with pivaloyl chloride (43 mg, 0.36 mmol) in the presence of CuCN (2.7 mg, 0.03 mmol) to afford **17** (81 mg, 44%) as colorless solid. R_f 0.62 (*E*/*P*=1:1); t_R 20.4 min (HP 5); mp 103 °C (E); $[\alpha]_D^{20}$ +58.6 (*c* 0.22, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (br s, 3H, (H_3C)(H_3C)CH–), 1.06 (s, 9H, H_3C–), 1.13 (br s, 3H, (H_3C)(H_3C)CH–), 1.24 (br d, ^3J=6.5 Hz, 6H, ($H_3C)_2CH$–), 3.69 (ps-s, 1H, ($H_3C)_2CH$–), 4.11 (ps-s, 1H, ($H_3C)_2CH$–), 7.13 (s, 1H, $H_{benzylic}$), 7.41–7.63 (m, 4H, H-2, H-3, H-6, H-7), 7.88–7.94 (m, 2H, H-4, H-5), 8.26 (dd, ^3J=8.4 Hz, ^4J=0.9 Hz, 1H, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (($H_3C)_2CH$–), 27.0 (($H_3C)_3C$–), 43.7 (($H_3C)_3C$–), 45.9 (($H_3C)_2CH$–), 73.7 ($C_{benzylic}$), 123.6, 125.1, 126.0, 126.9, 128.1, 128.8, 129.9, 130.3, 131.6, 134.2 (C-naph), 154.7 (NC═O), 211.2 (C-12); IR (KBr) 3055, 2970, 2934, 2872, 1716, 1687, 1598, 1512, 1477, 1437, 1368 cm^{-1}; MS (ESI) *m*/*z* 370.2405 $[M+H]^+$. Anal. Calcd for $C_{23}H_{31}NO_3$: C, 74.76; H, 8.46; N, 3.79. Found: C, 75.03; H, 8.55; N, 3.82.

6.3. Synthesis of indanoles 26

6.3.1. N,N-Diisopropylcarbamic acid (2-iodo-benzyl) ester (**18**)

According to the procedure for carbamoylation of primary benzyl carbamates described in Ref. 13, 2-iodo-benzyl alcohol (1.45 g, 6.00 mmol) was dissolved in 10.0 mL of dry THF and deprotonated using sodium hydride (263 mg, 6.90 mmol, suspension in mineral oil (60%)). *N*,*N*-Diisopropylcarbamic acid chloride (1.13 g, 6.90 mmol) was added. Work-up according to Ref. 13 and purification of the crude product by flash chromatography (*E*/*P*=1:4) yielded 1.70 g (78%) of benzyl carbamate **18** as slightly yellow solid. R_f 0.56 (*E*/*P*=1:1); t_R 15.7 min (HP 5); mp 55 °C (E); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, ^3J=6.9 Hz, 12H, ($H_3C)_2CH$–), 3.95

(ps-s, 2H, $(H_3C)_2CH$–), 5.14 (s, 2H, $H_{benzylic}$), 6.99 (ddd, ^3J=7.9, 7.6 Hz, ^4J=1.9 Hz, 1H, H-4), 7.33 (ddd, ^3J=7.9, 7.1 Hz, ^4J=1.1 Hz, 1H, H-5), 7.37 (dd, ^3J=7.1 Hz, ^4J=1.9 Hz, 1H, H-6), 7.84 (dd, ^3J=7.6 Hz, ^4J=1.1 Hz, 1H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9 ($(H_3C)_2CH$–), 46.0 ($(H_3C)_2CH$–), 70.3 ($C_{benzylic}$), 98.2 (C-2), 128.3 (C-6), 129.3 (C-4), 129.4 (C-5), 139.4 (C-3), 139.6 (C-1), 155.0 (NC=O); IR (ATR) 3070, 3060, 2982, 2964, 2925, 2872, 1692, 1567, 1534, 1471, 1446, 1425, 1377 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 361 (2) $[M]^+$, 346 (9) $[(M-CH_3)]^+$, 302 (21), 260 (3) $[(M-N^iPr_2)]^+$, 234 (45) $[(M-I)]^+$, 216 (100) $[(M-OCb)]^+$, 144 (8) $[OCb]^+$, 128 (13) $[Cb]^+$, 90 (25) $[C_7H_6]^+$. Anal. Calcd for $C_{14}H_{21}INO_2$: C, 46.42; H, 5.84; N, 3.87. Found: C, 46.65; H, 5.45; N, 3.77.

6.3.2. *N,N-Diisopropylcarbamic acid (2-tributylstannyl-benzyl) ester (**19**)*

In a flame-dried round bottom flask, carbamate **18** (1.81 g, 5.00 mmol) was dissolved in 20 mL of dry THF. The solution was cooled to −40 °C and isopropyl-magnesium chloride (2.5 mL of a 2 M solution in THF, 5.00 mmol) was added. When TLC shows complete iodo-magnesium exchange, tributyltin chloride (3.26 g, 10.00 mmol) was added and the reaction was allowed to warm to rt. Methanol (5 mL) and water (10 mL) were added and the resulting suspension was further diluted with 10 mL of TBME. The phases were separated, the aqueous phase was extracted with TBME (3×20 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography (*E*/*P*=1:20) yielded 2.07 g (79%) of **19** as colorless liquid. R_f 0.81 (*E*/*P*=1:1); t_R 20.9 min (HP 5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, ^3J=7.0 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.01–1.13 (m, 6H, $H_3CCH_2CH_2CH_2$–), 1.19 (d, ^3J=6.3 Hz, 12H, $(H_3C)_2CH$–), 1.23–1.38 (m, 6H, $H_3CCH_2CH_2CH_2$–), 1.44–1.62 (m, 6H, $H_3CCH_2CH_2CH_2$–), 3.85 (ps-s, 2H, $(H_3C)_2CH$–), 4.98 (s, 2H, $H_{benzylic}$), 7.18 (ddd, ^3J=7.7, 7.4 Hz, ^4J=1.4 Hz, 1H, H-5), 7.25 (ddd, ^3J=^3J=7.4 Hz, ^4J=1.6 Hz, 1H, H-4), 7.39–7.46 (m, 2H, H-3, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.3 ($H_3CCH_2CH_2CH_2$–), 13.5 ($H_3CCH_2CH_2CH_2$–), 21.0 ($(H_3C)_2CH$–), 27.1 (H_3CCH_2–CH_2CH_2–), 29.0 (H_3CCH_2–CH_2CH_2–), 45.9 ($(H_3C)_2CH$–), 69.1 ($C_{benzylic}$), 127.1, 128.3, 128.6 (C-4 to C-6), 136.6 (C-2), 142.1 (C-3), 143.5 (C-1), 155.2 (NC=O). IR (ATR) 3054, 2999, 2957, 2926, 2872, 2854, 1694, 1541, 1464, 1436, 1377, 1367 cm^{-1}; MS (ESI) *m*/*z* 526.2698 $[M+H]^+$. Anal. Calcd for $C_{26}H_{47}NO_2Sn$: C, 59.56; H, 9.03; N, 2.67. Found: C, 59.78; H, 9.32; N, 2.72.

6.3.3. *(E)-4-{2-[(N,N-Diisopropylcarbamoyloxy)-methyl]-phenyl}-but-2-enoic acid methyl ester (**20**)*

$Pd_2(dba)_3$ (457 mg, 0.50 mmol) was suspended in 10.0 ml of dry DMF in a flame-dried Schlenk tube under argon atmosphere. *trans*-4-Bromo-crotonic acid methyl ester (1.34 g, 7.50 mmol) was added and the mixture was stirred for 30 min. Then, stannane **19** (2.62 g, 5.00 mmol) was injected and the stirred reaction mixture was heated to 60 °C for 60 h (sealed tube conditions). After cooling down to rt, 10 mL of brine were added, followed by 10 mL of TBME. The organic layer was separated and the aqueous one was extracted with TBME (3×15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography on silica gel (*E*/*P*=1:6→1:1) afforded pure ester (*E*)-**20** (1.43 g, 86%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.59 (*E*/*P*=1:1); t_R 20.2 min (HP 5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (br d, ^3J=7.3 Hz, 12H, $(H_3C)_2CH$–), 3.56 (dd, ^3J=6.6 Hz, ^4J=1.7 Hz, 2H, –CH_2CH=CH–), 3.64 (s, 3H, –OCH_3), 3.83 (ps-s, 2H, $(H_3C)_2CH$–), 5.05 (s, 2H, $H_{benzylic}$), 5.66 (dt, ^3J=15.8 Hz, ^4J=1.7 Hz, 1H, –CH_2CH=C*H*–), 7.05 (dt, ^3J=15.8, 6.6 Hz, 1H, –CH_2CH=CH–), 7.10 (dd, ^3J=5.8 Hz, ^4J=2.5 Hz, 1H, H-6), 7.16–7.27 (m, 2H, H-4, H-5), 7.64 (dd, ^3J=6.6 Hz, ^4J=2.6 Hz, 1H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7 ($(H_3C)_2CH$–), 34.9 (–CH_2CH=CH–), 45.8 ($(H_3C)_2CH$–), 51.4 (–OCH_3), 64.2 ($C_{benzylic}$), 122.0 (–CH_2CH=C*H*–), 127.0 (C-4), 128.5 (C-3), 129.8 (C-5), 130.0 (C-6), 135.0 (C-1), 136.2 (C-2), 147.2 (–CH_2CH=CH–), 155.1 (NC=O), 166.8 (C=O); IR (ATR) 3067, 3032, 2966, 2927, 2871, 2852, 1683, 1671, 1601, 1559, 1474, 1446, 1436, 1376 cm^{-1}; MS (ESI) *m*/*z* 356.1833 $[M+Na]^+$. Anal. Calcd for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20. Found: C, 68.16; H, 8.22; N, 4.10.

6.3.4. *(E)-N,N-Diisopropylcarbamic acid 2-(4-hydroxy-but-2-enyl)-benzyl ester (**21**)*

α,β-Unsaturated ester **20** (47 mg, 0.14 mmol) was dissolved in dry THF and the solution was cooled down to −78 °C. DIBAL-H (0.35 mL of a 1 M solution in toluene, 0.35 mmol) was slowly added and the reaction mixture was stirred until the starting material was fully consumed (2 h, TLC control). Methanol of 2 mL were carefully added, followed by 2 mL of water before the reaction mixture was allowed to warm to rt slowly. At rt 5 mL of TBME were used for dilution and 2 N HCl were added until the solution became clear. The phases were separated and the organic layer was extracted with TBME (3×10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography on silica gel (*E*/*P*=1:1) yielded allyl alcohol (*E*)-**21** (36 mg, 84%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.13 (*E*/*P*=1:1); t_R 21.7 min (HP 5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (d, ^3J=6.8 Hz, 12H, $(H_3C)_2CH$–), 1.91 (brps-s, 1H, O*H*), 3.39 (dd, ^3J=6.4 Hz, ^4J=0.9 Hz, 2H, –CH_2CH=$CHCH_2O$–), 3.85 (ps-s, 2H, $(H_3C)_2CH$–), 4.02 (ddd, ^3J=5.9, 2.5 Hz, ^4J=1.2 Hz, 2H, –CH_2CH=$CHCH_2O$–), 5.09 (s, 2H, $H_{benzylic}$), 5.56 (dtd, ^3J=5.9, 15.3 Hz, ^4J=1.2 Hz, 1H, –CH_2–CH=C*H*CH_2O–), 5.76 (dtd, ^3J=15.3, 6.4 Hz, ^4J=1.2 Hz, 1H, –CH_2CH=$CHCH_2O$–), 7.12 (dd, ^3J=7.1 Hz, ^4J=2.0 Hz, 1H, H-3), 7.16 (ddd, ^3J=^3J=7.0 Hz, ^4J=2.0 Hz, 1H, H-5), 7.20 (ddd, ^3J=7.1, 7.0 Hz, ^4J=1.9 Hz, 1H, H-4), 7.30 (dd, 1H, ^3J=7.0 Hz, ^4J=1.9 Hz, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8 ($(H_3C)_2CH$–), 35.5 (–CH_2CH=CH–CH_2O–), 45.7 ($(H_3C)_2CH$–), 63.5 ($C_{benzylic}$), 64.1 (–CH_2CH=$CHCH_2O$–), 126.6, 128.2, 129.1, 129.7, 130.6 (–CH_2CH=C*H*–CH_2O–, C-3, C-4, C-5, C-6), 135.0 (C-2), 138.1 (C-1), 155.3 (NC=O); IR (ATR) 3431, 3067, 3033, 2997, 2970, 2934, 2874, 1680, 1605, 1477, 1439, 1369 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{27}NO_3$: *m*/*z* 328.1883 $[M+Na]^+$, found: *m*/*z* 328.1887 $[M+Na]^+$.

6.3.5. *(E)-N,N-Diisopropylcarbamic acid 2-[4-(tert-butyl-dimethylsilanyloxy)-but-2-enyl]-benzyl ester (**22**)*

Allyl aclcohol (*E*)-**21** (360 mg, 1.18 mmol) was dissolved in 5.0 mL of dry THF. Triethylamine (0.48 g, 4.13 mmol) and a catalytic amount of DMAP were added at rt. The mixture was stirred until it became clear. After cooling to 0 °C, *tert*-butyl-dimethylsilyl chloride (214 mg, 1.42 mmol) was added and the reaction mixture was stirred for 12 h at rt. Dilution by TBME (10 mL) was followed by addition of water (10 mL). The phases were separated and the aqueous one was extracted with TBME (3×10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography yielded silyl ether (*E*)-**22** (334 mg, 67%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.72 (*E*/*P*=1:1), t_R 21.8 min (HP 5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 6H, $(H_3C)_3C(CH_3)_2Si$–), 0.84 (s, 9H, $(H_3C)_3C(CH_3)_2Si$–), 1.16 (d, ^3J=6.6 Hz, 12H, $(H_3C)_2CH$–), 3.41 (dd, ^3J=6.4 Hz, ^4J=1.3 Hz, 2H, –CH_2CH=$CHCH_2O$–), 3.88 (ps-s, 2H, $(H_3C)_2CH$–), 4.09 (dd, ^3J=5.2 Hz, ^4J=1.4 Hz, 2H, –CH_2CH=$CHCH_2O$–), 5.10 (s, 2H, $H_{benzylic}$), 5.49 (tdt, ^3J=15.4, 5.2 Hz, ^4J=1.3 Hz, 1H, –CH_2CH=C*H*CH_2O–), 5.76 (tdt, ^3J=5.2, 6.4 Hz, ^4J=1.4 Hz, 1H, –CH_2–C*H*=$CHCH_2O$–), 7.12–7.26 (m, 3H, H-3 to H-5), 7.32 (dd, ^3J=7.4 Hz, ^4J=1.8 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.4 ($(H_3C)_3C(CH_3)_2Si$–), 18.1 ($(H_3C)_3C$–$(CH_3)_2Si$–), 21.0 ($(H_3C)_2CH$–), 25.8 ($(H_3C)_3C(CH_3)_2Si$–), 35.0 (–CH_2CH=$CHCH_2O$–), 45.8 ($(H_3C)_2CH$–), 63.6 (–CH_2CH=$CHCH_2O$–), 64.2 ($C_{benzylic}$), 126.3 (–CH_2CH=CH–CH_2O–), 128.1 (C-5), 128.7 (C-6), 129.2 (C-4), 129.5 (C-3), 130.9 (–CH_2CH=C*H*CH_2O–), 134.8 (C-2), 138.6 (C-1), 155.3 (NC=O); IR (ATR) 3067, 2957, 2929, 2872, 2856, 1696, 1670, 1654, 1616, 1559, 1464, 1437, 1377 cm^{-1}; MS (ESI) *m*/*z* 442.2745 $[M+Na]^+$. Anal. Calcd for $C_{24}H_{41}NO_3Si$: C, 68.69; H, 9.85; N, 3.34. Found: C, 68.52; H, 10.06; N, 3.20.

*6.3.6. (−)-(S)-(E)-N,N-Diisopropylcarbamic acid {2-[4-(tert-butyl-dimethylsilanyloxy)-but-2-enyl]-phenyl}-tributylstannyl-methyl ester (**23**)*

Silyl ether **22** (267 mg, 0.62 mmol) and bis(oxazoline) (−)-(*S*,*S*)-**27** (300 mg, 0.93 mmol) were dissolved in 5 mL of dry diethyl ether in a flame-dried round bottom flask under argon atmosphere. This solution was cooled to −78 °C and *sec*-butyllithium (0.76 mL, 1.22 M, 0.93 mmol) was added slowly. The reaction mixture was stirred at this temperature for 2.5 h before tributyltin chloride (303 mg, 0.93 mmol) was injected. Stirring was continued for 3 h at −78 °C. Then 1.0 mL of methanol, 1.0 mL of water, and 1.0 mL of 2 N HCl were added, and the mixture was allowed to warm to rt. Further dilution with TBME (10 mL) and water (10 mL) was followed by separation of phases and extraction of the aqueous phase with TBME (3×10 mL). The combined organic layers were washed with satd $NaHCO_3$ and dried over $MgSO_4$ prior to concentration in vacuo. Flash chromatography on silica gel (*E*/*P*=1:30) afforded stannane (−)-(*S*)-(*E*)-**23** (425 mg, 95%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f=0.85 (*E*/*P*=1:1); t_R 24.7 min+decomposition (HP 5); $[\alpha]_D^{20}$ −54.4 (*c* 1.02, $CHCl_3$), 97% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 6H, $(H_3C)_3C(CH_3)_2Si$–), 0.76 (t, ^3J=7.6 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 0.84 (s, 9H, $(H_3C)_3C(CH_3)_2Si$–), 1.08–1.34 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.17 (d, ^3J=7.0 Hz, 12H, $(H_3C)_2CH$–), 3.13 (dd, ^2J=15.8 Hz, ^3J=6.4 Hz, 1H, –CH_AH_BCH=CHCH$_2$O–), 3.25 (dd, ^3J=6.4 Hz, ^2J=15.8 Hz, 1H, –CH_AH_BCH=CHCH$_2$O–), 3.91 (sept, ^3J=7.0 Hz, 2H, $(H_3C)_2CH$–), 4.11 (dd, ^3J=5.0 Hz, ^4J=1.4 Hz, 2H, –CH_AH_B–CH=CHCH_2O–), 5.55 (tdt, ^3J=15.4, 5.0 Hz, ^4J=1.4 Hz, 1H, –CH_AH_B–CH=CHCH$_2$O–), 5.76 (s, 1H, $H_{benzylic}$), 5.77 (tdt, ^3J=15.4 Hz, ^4J=1.4 Hz, ^3J=6.4 Hz, 1H, –CH_AH_BCH=CHCH$_2$O–), 6.97 (dd, ^3J=7.4 Hz, ^4J=1.4 Hz, 1H, H-3), 7.03 (ddd, ^3J=7.6, 7.5 Hz, ^4J=1.4 Hz, 1H, H-5), 7.11 (ddd, ^3J=7.4, 7.6 Hz, ^4J=1.2 Hz, 1H, H-4), 7.22 (dd, ^3J=7.5 Hz, ^4J=1.2 Hz, 1H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.4 ($(H_3C)_3C(CH_3)_2Si$–), 10.5 ($H_3CCH_2CH_2CH_2$–), 13.4 ($H_3CCH_2CH_2CH_2$–), 18.1 ($(H_3C)_3C$–$(CH_3)_2Si$–), 21.0 ($(H_3C)_2CH$–), 25.8 ($(H_3C)_3C(CH_3)_2Si$–), 27.4 ($H_3CCH_2CH_2CH_2$–), 28.6 ($H_3CCH_2CH_2CH_2$–), 35.0 (–CH_AH_BCH=CHCH$_2$O–), 45.5 ($(H_3C)_2CH$–), 63.6 (–CH_AH_BCH=CHCH$_2$O–), 71.8 ($C_{benzylic}$), 124.6 (–CH_AH_B–CH=CHCH$_2$O–), 124.7 (C-5), 126.3 (C-6), 128.4 (C-4), 128.7 (C-3), 131.3 (–CH_AH_BCH=CHCH$_2$O–), 133.5 (C-2), 141.1 (C-1), 155.4 (NC=O); IR (ATR) 3067, 2957, 2926, 2872, 2855, 1679, 1600, 1501, 1463, 1442, 1433, 1378 cm^{-1}; MS (ESI) *m*/*z* 732.3801 $[M+Na]^+$. Anal. Calcd for $C_{36}H_{67}NO_3SiSn$: C, 61.01; H, 9.53; N, 1.98. Found: C, 60.78; H, 9.37; N, 1.84.

*6.3.7. (+)-(S)-(E)-N,N-Diisopropylcarbamic acid 1-[2-(4-hydroxy-but-2-enyl)-phenyl]-1-tributylstannyl-methyl ester (**24**)*

Stannylated silyl ether **23** (212 mg, 0.30 mmol) was dissolved in a mixture of 2 mL THF and 3 mL diethyl ether. The solution was cooled to 0 °C and tetrabutyl-ammonium chloride (0.9 mL, 1 M solution in THF, 0.90 mmol) was added. The solution was stirred at 0 °C until TLC-monitoring proved complete conversion of the starting material. The solution was then diluted with 10 mL of brine and 5 mL of TBME. The phases were separated, the aqueous one was extracted with TBME (3×10 mL), and the combined organic phases were dried over $MgSO_4$ prior to concentration in vacuo. Flash chromatography on silica gel afforded pure stannylated allyl alcohol (+)-(*S*)-(*E*)-**24** (145 mg, 81%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.36 (*E*/*P*=1:1); $[\alpha]_D^{20}$ +25.5 (*c* 1.00, $CHCl_3$); HPLC: Chiralcel AD-H (4.6×250 mm), H/^{i}PrOH=200:1, 1.0 mL min^{-1}, λ 210 nm, t_R(−) 31.1 min, t_R(+) 38.8 min, 97% ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (t, ^3J=7.4 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.13–1.44 (m, 30H, $(H_3C)_2CH$–, $H_3CCH_2CH_2CH_2$–), 2.45 (t, ^3J=5.7 Hz, 1H, O*H*), 3.20 (dd, ^2J=16.0 Hz, ^3J=5.1 Hz, 1H, –CH_AH_BCH=CHCH$_2$O–), 3.27 (dd, ^2J=16.0 Hz, ^3J=7.0 Hz, 1H, –CH_AH_BCH=CHCH$_2$O–), 3.83 (ps-s, 1H, $(H_3C)_2CH$–), 3.99–4.13 (m, 3H, $(H_3C)_2CH$–, –CH_AH_BCH=CHCH_2O–), 5.66 (dtd, ^3J=15.4, 6.3 Hz, ^4J=1.3 Hz, 1H, –CH_AH_BCH=CH–CH$_2$O), 5.76–5.84 (m, 1H, –CH_AH_BCH=CH–CH$_2$O), 6.13 (s, 1H, $H_{benzylic}$), 7.00–7.08 (m, 2H, H-3, H-5), 7.18 (ddd, ^3J=7.0, 7.7 Hz, ^4J=1.6 Hz, 1H, H-4), 7.24 (dd, ^3J=7.8 Hz, ^4J=1.6 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1 ($H_3CCH_2CH_2CH_2$–), 13.6 ($H_3CCH_2CH_2CH_2$–), 20.9 ($(H_3C)_2CH$–), 27.4 ($H_3CCH_2CH_2CH_2$–), 28.8 (H_3CCH_2–CH_2CH_2–), 36.2 (–CH_AH_BCH=CHCH$_2$O–), 46.0 ($(H_3C)_2CH$–), 63.8 (–CH_AH_BCH=CH–CH$_2$O–), 70.8 ($C_{benzylic}$), 124.6 (CH_AH_B–CH=CHCH$_2$O–), 124.9 (C-5), 126.7 (C-6), 129.5 (C-4), 130.7 (C-3), 130.9 (CH_AH_B–CH=CHCH$_2$O–), 132.6 (C-2), 142.2 (C-1), 155.2 (NC=O); IR (ATR) 3426, 3023, 2997, 2971, 2939, 2879, 2843, 1734, 1684, 1474, 1464, 1437, 1369 cm^{-1}; MS (ESI) *m*/*z* 618.2946 $[M+Na]^+$. Anal. Calcd for $C_{30}H_{53}NO_3Sn$: C, 60.61; H, 8.99; N, 2.36. Found: C, 60.98; H, 8.81; N, 2.18.

*6.3.8. (−)-(S)-(E)-N,N-Diisopropylcarbamic acid [2-(4-bromo-but-2-enyl)-phenyl]-tributylstannyl-methyl ester (**25**)*

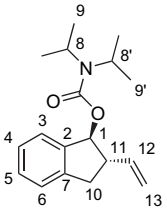
Allyl alcohol **24** (105 mg, 0.19 mmol) was dissolved in 5 mL of dry dichloromethane. Tetrabromomethane (79 mg, 0.23 mmol) was added and the mixture was cooled to 0 °C before triphenylphosphin (76 mg, 0.29 mmol) was added portion wise. The reaction mixture was stirred for 1 h at 0 °C. Diethyl ether (30 mL) was added and the resulting suspension was stirred for additional 30 min and thereby warmed to rt. The residue was filtered through a pad of silica gel and the filtrate was concentrated in vacuo. Purification by flash chromatography afforded allyl bromide derivative (−)-(*S*)-(*E*)-**25** (92 mg, 74%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.71 (*E*/*P*=1:1); $[\alpha]_D^{20}$ −62.4 (*c* 1.00, $CHCl_3$), 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, ^3J=7.1 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.14–1.41 (m, 18H, $H_3CCH_2CH_2$–CH_2–), 1.23 (d, ^3J=6.8 Hz, 12H, $(H_3C)_2CH$–), 3.23 (dd, ^2J=16.1 Hz, ^3J=7.1 Hz, 1H, –CH_AH_B–CH=CHCH$_2$Br), 3.34 (dd, ^3J=6.5 Hz, ^2J=16.1 Hz, 1H, –CH_AH_BCH=CH–CH$_2$Br), 4.95 (sept, ^3J=6.8 Hz, 2H, H-8), 4.96 (d, ^3J=7.4 Hz, 2H, –CH_AH_BCH=CHCH$_2$Br), 5.75 (tdt, ^3J=15.2, 7.6 Hz, ^4J=1.3 Hz, 1H, –CH_AH_BCH=CH–CH$_2$Br), 5.80 (s, 1H, $H_{benzylic}$), 5.90–5.98 (m, 1H, –CH_AH_B–CH=CHCH$_2$Br), 7.02–7.09 (m, 2H, H-3, H-5), 7.19 (ddd, ^3J=6.0, 7.6 Hz, ^4J=2.7 Hz, 1H, H-4), 7.28 (ps-d, ^3J=8.0 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5 ($H_3CCH_2CH_2CH_2$–), 13.5 ($H_3CCH_2CH_2CH_2$–), 21.0 ($(H_3C)_2CH$–), 27.5 (H_3CCH_2–CH_2CH_2–), 28.9 (H_3CCH_2–CH_2CH_2–), 32.9 (–CH_AH_B–CH=CHCH$_2$Br), 35.1 (–CH_AH_B–CH=CHCH$_2$Br), 45.8 ($(H_3C)_2CH$–), 71.6 ($C_{benzylic}$), 125.0 (–CH_AH_BCH=CH–CH$_2$Br), 125.1 (C-5), 126.7 (C-6), 128.0 (C-4), 129.0 (C-3), 132.6 (C-2), 133.8 (–CH_AH_BCH=CHCH$_2$Br), 141.4 (C-1), 155.4 (NC=O); IR (ATR) 3066, 2957, 2925, 2871, 2853, 1679, 1600, 1483, 1478, 1462, 1438, 1377 cm^{-1}; MS (ESI) *m*/*z* 680.2092 $[M+Na]^+$. Anal. Calcd for $C_{30}H_{52}BrNO_2Sn$: C, 54.81; H, 7.97; N, 2.13. Found: C, 55.04; H, 8.16; N, 2.03.

*6.3.9. N,N-Diisopropylcarbamic acid (2,3-dihydro-2-vinyl-1H-inden-1-yl) ester (**26**)*

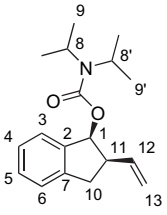
According to GPA, CuCN (2.5 mg, 0.03 mmol) was suspended in 1 mL of dry toluene and allyl bromide derivative **25** (92 mg, 0.14 mmol) was added. The mixture was stirred for 72 h at 70 °C under sealed tube conditions. Work-up was performed as outlined in GPA. The crude product was subjected to flash chromatography on silica gel (*E*/*P*=1:20) to yield separately *trans*-**26** (17 mg, 42%) and *cis*-**26** (17 mg, 42%).

(−)-(*S*,*S*)-**26** (*trans*-**26**): R_f 0.48 (*E*/*P*=1:4); t_R 16.61 min (HP 5); 21.12 min (HP 1701); $[\alpha]_D^{20}$ −65.1 (*c* 0.32, $CHCl_3$); HPLC: CHIRAGROM 1 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(−) 11.1 min, t_R(+) 12.6 min, 98% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (d, ^3J=6.9 Hz, 6H, H-9), 1.17 (d, ^3J=6.9 Hz, 6H, H-9′), 2.73 (dd, ^2J=18.7 Hz, ^3J=5.6 Hz, 1H, H_A-10), 3.06 (dddt, ^3J=6.7, 7.8, 7.6 Hz, ^4J=1.0 Hz, 1H, H-11), 3.10 (dd, ^2J=18.7 Hz, ^3J=7.8 Hz, 1H, H_B-10), 3.65 (ps-s, 1H, H-8), 4.15 (ps-s, 1H, H-8′), 5.03 (ddd, ^2J=1.6 Hz, ^3J=10.3 Hz, ^4J=1.0 Hz, 1H, H_{cis}-13), 5.12 (ddd, ^2J=1.6 Hz, ^3J=17.2 Hz, ^4J=1.0 Hz, 1H, H_{trans}-13), 5.96 (ddd, ^3J=17.2, 10.3, 7.6 Hz, 1H, H-12), 6.04 (d, 1H, H-1), 7.11–7.23 (m, 3H, H-4, H-5, H-6), 7.28 (ps-d, ^3J=6.7 Hz, 1H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2 (C-9, C-9′), 35.9

(C-10), 45.8 (C-8, C-8′), 51.3 (C-11), 81.8 (C-1), 115.6 (C-13), 124.5 (C-4), 124.9 (C-3), 126.7 (C-5), 128.2 (C-6), 138.9 (C-12), 141.7(7) (C-7), 141.7(9) (C-2), 155.8 (NC=O); IR (ATR) 3076, 2997, 2969, 2932, 2874, 2853, 1687, 1643, 1478, 1462, 1433, 1368 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{25}NO_2$: *m*/*z* 310.1778 $[M+Na]^+$, found: *m*/*z* 310.1783 $[M+Na]^+$.



(−)-(*S*,*R*)-**26** (*cis*-**26**): R_f 0.41 (*E*/*P*=1:4); t_R 16.59 min (HP 5); 21.09 min (HP 1701); $[\alpha]_D^{20}$ −49.2 (*c* 0.31, $CHCl_3$); HPLC: CHIRAGROM 1 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(−) 13.2 min, t_R(+) 20.4 min, 70% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (br ps-s, 12H, H-9, H-9′), 2.98 (dd, ^2J=12.2 Hz, ^3J=7.2 Hz, 1H, H_B-10), 3.03 (m, 1H, H_A-10), 3.27 (dddt, ^3J=6.2 Hz, ^3J=^3J=7.2 Hz, ^4J=1.2 Hz, 1H, H-11), 3.64 (ps-s, 1H, H-8), 4.01 (ps-s, 1H, H-8′), 5.03 (ddd, ^2J=1.9 Hz, ^3J=10.3 Hz, ^4J=1.2 Hz, 1H, H_{cis}-13), 5.13 (ddd, ^2J=1.9 Hz, ^3J=17.3 Hz, ^4J=1.2 Hz, 1H, H_{trans}-13), 5.89 (ddd, ^3J=7.2, 10.3, 17.3 Hz, 1H, H-12), 6.11 (d, ^3J=6.2 Hz, 1H, H-1), 7.13–7.32 (m, 3H, H-4, H-5, H-6), 7.40 (ps-d, ^3J=7.3 Hz, 1H, H-3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7 (C-9, C-9′), 36.2 (C-10), 45.8 (C-8, C-8′), 48.0 (C-11), 79.1 (C-1), 116.1 (C-13), 124.6 (C-4), 125.7 (C-3), 126.6 (C-5), 128.6 (C-6), 137.2 (C-12), 141.6 (C-7), 142.9 (C-2), 155.3 (NC=O); IR (ATR) 3076, 2969, 2933, 2875, 1685, 1642, 1477, 1462, 1433, 1368 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{25}NO_2$: *m*/*z* 310.1778 $[M+Na]^+$, found: *m*/*z* 310.1771 $[M+Na]^+$.



6.4. Synthesis of indanoles 36

*6.4.1. N,N-Diisopropylcarbamic acid 6-iodo-benzo[1,3]dioxol-5-ylmethyl ester (**28**)*

According to the synthesis of benzyl carbamate **18**, (6-iodo-benzo[1,3]dioxol-5-yl)-methanol (10.50 g, 38 mmol) was dissolved in 120 mL of THF and deprotonated by sodium hydride (1.75 g, 43.70 mmol, suspension in mineral oil (60%)). Trapping with *N*,*N*-diisopropylcarbamoyl chloride (7.15 g, 43.70 mmol), work-up, and purification by flash chromatography on silica gel (*E*/*P*=1:4) afforded benzyl carbamate **28** (10.3 g, 67%) as slightly yellow solid. R_f 0.57 (*E*/*P*=1:1); t_R 20.8 min (HP 5); mp 71 °C (E); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (d, ^3J=6.9 Hz, 12H, $(H_3C)_2CH$–), 3.82 (ps-s, 1H, $(H_3C)_2CH$–), 3.99 (ps-s, 1H, $(H_3C)_2CH$–), 5.04 (s, 2H, $H_{benzylic}$), 5.96 (s, 2H, –CH_2–), 6.90 (s, 1H, H-2), 7.24 (s, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0 ($(H_3C)_2CH$–), 46.0 ($(H_3C)_2CH$–), 70.3 ($C_{benzylic}$), 86.8 (C-6), 101.7 (–CH_2–), 110.0 (C-2), 118.7 (C-5), 132.9 (C-1), 148.2 (C-3), 148.4 (C-4), 155.1 (NC=O); IR (ATR) 3093, 2968, 2933, 2901, 1689, 1663, 1610, 1502, 1477, 1444, 1431, 1412, 1387, 1368 cm^{-1}; MS (ESI) *m*/*z* 428.0329 $[M+Na]^+$. Anal. Calcd for $C_{15}H_{20}INO_4$: C, 44.46; H, 4.97; N, 3.46. Found: C, 44.30; H, 4.77; N, 3.28.

*6.4.2. N,N-Diisopropylcarbamic acid 6-tributylstannyl-benzo[1,3]dioxol-5-ylmethyl ester (**29**)*

To a solution of *n*-butylmagnesium chloride (11.00 mL of an 1 M solution in THF, 11.00 mmol) in 40 mL of dry THF, *n*-butyllithium (13.80 mL of an 1.6 M solution in hexane, 22.00 mmol) was added at 0 °C. The solution is stirred for 10 min before it was cooled to −78 °C. Benzyl carbamate **28** (4.05 g, 10.00 mmol), dissolved in 10 mL of dry THF, was added dropwise and the mixture was stirred for 2 h. Then tributyltin chloride (7.15 g, 22.00 mmol) was injected and the reaction was stirred for 4 h during which it was slowly warmed to rt. Work-up was managed according to the synthesis of stannane **19**. Purification by flash chromatography (*E*/*P*=1:20→1:15) yielded stannane **29** (2.51 g, 44%) as colorless liquid. R_f 0.67 (*E*/*P*=1:1); t_R 24.9 min (HP 5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, ^3J=6.9 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 0.99–1.10 (m, 6H, $H_3CCH_2CH_2CH_2$–), 1.18 (ps-s, 12H, $(H_3C)_2CH$–), 1.21–1.35 (m, 6H, $H_3CCH_2CH_2CH_2$–), 1.40–1.56 (m, 6H, $H_3CCH_2CH_2CH_2$–), 3.89 (ps-s, 2H, $(H_3C)_2CH$–), 4.93 (s, 2H, $H_{benzylic}$), 5.92 (s, 2H, –CH_2–), 6.86 (s, 1H, H-2), 6.94 (s, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.4 ($H_3CCH_2CH_2CH_2$–), 13.7 ($H_3CCH_2CH_2CH_2$–), 21.0 ($(H_3C)_2CH$–), 27.3 ($H_3CCH_2CH_2CH_2$–), 29.0 ($H_3CCH_2CH_2$–CH_2–), 45.9 ($(H_3C)_2CH$–), 69.1 ($C_{benzylic}$), 100.7 (–CH_2–), 109.9 (C-2), 114.9 (C-5), 134.6 (C-6), 137.1 (C-1), 147.1 (C-3), 148.1 (C-4), 155.3 (NC=O); IR (ATR) 3055, 2957, 2926, 2872, 2854, 1691, 600, 1503, 1477, 1440, 1377 cm^{-1}; MS (ESI) *m*/*z* 592.2420 $[M+Na]^+$. Anal. Calcd for $C_{27}H_{47}NO_4Sn$: C, 57.06; H, 8.33; N, 2.46. Found: C, 56.98; H, 8.47; N, 2.36.

*6.4.3. (E)-4-{6-[(N,N-Diisopropylcarbamoyloxy)-methyl]-benzo[1,3]dioxol-5-yl}-but-2-enoic acid methyl ester (**30**)*

According to the synthesis of ester **20**, stannane **29** (2.27 g, 4.00 mmol) was coupled with *trans*-4-bromo-crotonic acid methyl ester (895 mg, 5.00 mmol) using $Pd_2(dba)_3$ (366 mg, 0.40 mmol) as catalyst and dry DMF (10.0 mL) as solvent. Flash chromatography on silica gel (*E*/*P*=1:6→1:2) afforded ester (*E*)-**30** (1.48 g, 98%) as colorless oil, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.36 (*E*/*P*=1:1); t_R 22.8 min (HP 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (ps-s, 12H, $(H_3C)_2CH$–), 3.50 (dd, ^3J=6.2 Hz, ^4J=1.8 Hz, 2H, –CH_2–CH=CH–), 3.66 (s, 3H, –OCH_3), 3.84 (ps-s, 2H, $(H_3C)_2CH$–), 4.96 (s, 2H, $H_{benzylic}$), 5.67 (dt, ^3J=15.7 Hz, ^4J=1.8 Hz, 1H, –CH_2CH=CH–), 5.91 (s, 2H, –CH_2–), 6.59 (s, 1H, H-2), 6.84 (s, 1H, H-5), 7.03 (dt, ^3J=6.2, 15.7 Hz, 1H, –CH_2CH=CH–); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7 ($(H_3C)_2CH$–), 34.6 (–CH_2CH=CH–), 45.6 ($(H_3C)_2CH$–), 51.2 (–OCH_3), 63.8 ($C_{benzylic}$), 101.0 (–CH_2–), 110.0 (C-5), 110.2 (C-2), 121.8 (–CH_2CH=CH–), 127.5 (C-1), 130.0 (C-6), 146.5 (C-4), 147.3 (–CH_2CH=CH–), 147.6 (C-3), 155.1 (NC=O), 166.7 (C=O); IR (ATR) 3067, 2970, 2902, 2846, 1721, 1684, 1655, 1505, 1488, 1436, 1377, 1369 cm^{-1}; MS (ESI) *m*/*z* 400.1731 $[M+Na]^+$. Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.64; H, 7.21; N, 3.71. Found: C, 63.61; H, 7.29; N, 3.48.

*6.4.4. (E)-N,N-Diisopropylcarbamic acid {1-[6-(4-hydroxybut-2-enyl)-benzo[1.3]dioxo-5-yl-methyl} ester (**31**)*

According to the synthesis of allyl alcohol **21**, ester **30** (189 mg, 0.50 mmol) was reduced by means of DIBAL-H (1.25 mL of an 1 M solution in toluene, 1.25 mmol) in 5.0 mL of dry THF at −78 °C. Flash chromatography on silica gel afforded allyl alcohol **31** (141 mg, 81%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.07 (*E*/*P*=1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, ^3J=7.0 Hz, 12H, $(H_3C)_2CH$–), 1.88 (ps-s, 1H, O*H*), 3.34 (dd, ^3J=6.2 Hz, ^4J=1.2 Hz, 2H, –CH_2CH=$CHCH_2O$–), 3.80 (ps-s, 1H, $(H_3C)_2CH$–), 3.97 (ps-s, 1H, $(H_3C)_2CH$–), 4.06 (dd, ^3J=5.8 Hz, ^4J=1.2 Hz, 2H, –CH_2CH=$CHCH_2O$–), 5.02 (s, 2H, $H_{benzylic}$), 5.60 (tdt, ^3J=15.4 Hz, ^4J=1.2 Hz, ^3J=5.8 Hz, 1H, –CH_2CH=$CHCH_2O$–), 5.76 (tdt, ^3J=15.4, 6.2 Hz, ^4J=1.2 Hz, 1H, –CH_2CH=$CHCH_2O$–), 5.91 (s, 2H, –CH_2–), 6.65 (s, 1H, H-5), 6.83 (s, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7 ($(H_3C)_2CH$–), 35.0 (–CH_2CH=$CHCH_2O$–), 45.6 ($(H_3C)_2CH$–), 63.1 ($C_{benzylic}$), 63.7 (–CH_2CH=$CHCH_2O$–), 100.9 (–CH_2–), 109.6 (C-2), 109.8 (C-5), 128.1 (–CH_2CH=CH–CH_2O–), 130.5 (C-7), 130.7 (–CH_2CH=$CHCH_2O$–), 132.0 (C-1), 146.0 (C-3), 147.4 (C-4), 155.5

(NC=O); IR (ATR) 3432, 3034, 2970, 2934, 2896, 1678, 1621, 1503, 1486, 1442, 1369 cm^{-1}; MS (ESI) *m/z* 372.1776 $[M+Na]^+$. Anal. Calcd for $C_{19}H_{27}NO_4$: C, 65.31; H, 7.79; N, 4.01 Found: C, 65.42; H, 8.07; N, 3.75.

*6.4.5. (E)-N,N-Diisopropylcarbamic acid {1-[6-(4-triethylsilanyl-oxy-but-2-enyl)-benzo[1,3]dioxol-5-yl]-methyl} ester (**32**)*

According to the synthesis of silyl ether **22**, allyl alcohol **31** (1.05 g, 3.00 mmol), dissolved in 30 mL of dry THF, was treated with triethylamine (756 mg, 7.50 mmol) and a catalytic amount of DMAP at 0 °C for 10 min. Triethylsilyl chloride (475 mg, 3.15 mmol) was injected dropwise and the reaction mixture was stirred for 12 h while warming to rt. Work-up as described in the synthesis of **22** and purification of the crude product by flash chromatography on silica gel (*E*/*P*=1.8) afforded silyl ether (*E*)-**32** (1.12 g, 80%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.69 (*E*/*P*=1:1); t_R 24.9 min (HP 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59 (q, ^3J=8.1 Hz, 6H, H_3CCH_2–), 0.94 (t, ^3J=8.1 Hz, 9H, H_3CCH_2–), 1.18 (d, ^3J=6.2 Hz, 12H, $(H_3C)_2$–CH–), 3.35 (dd, ^3J=6.5 Hz, ^4J=1.3 Hz, 2H, –CH_2CH=CH–CH_2O–), 3.80 (ps-s, 1H, $(H_3C)_2CH$–), 3.99 (ps-s, 1H, $(H_3C)_2CH$–), 4.11 (dd, ^3J=5.3 Hz, ^4J=1.3 Hz, 2H, –CH_2CH=CHCH_2O–), 5.01 (s, 2H, $H_{benzylic}$), 5.53 (tdt, ^3J=15.3, 5.3 Hz, ^4J=1.3 Hz, 1H, –CH_2CH=CHCH$_2$O–), 5.75 (tdt, ^3J=15.3, 6.5 Hz, ^4J=1.3 Hz, 1H, –CH_2CH=CH–CH_2O–), 5.92 (s, 2H, –CH_2–), 6.67 (s, 1H, H-5), 6.84 (s, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2 (H_3CCH_2–), 6.4 (H_3CCH_2–), 20.8 ($(H_3C)_2$CH–), 34.6 (–CH_2CH=CHCH_2O–), 45.4 ($(H_3C)_2$CH–), 63.2 (–CH_2CH=CHCH_2O–), 63.9 ($C_{benzylic}$), 100.7 (–CH_2–), 109.7 (C-2), 109.8 (C-5), 127.9 (–CH_2CH=CHCH_2O–), 129.2 (C-6), 130.7 (–CH_2CH=CHCH$_2O$–), 132.6 (C-1), 145.8 (C-3), 147.3 (C-4), 155.5 (NC=O); IR (ATR) 3037, 2957, 2936, 2911, 2876, 1689, 1622, 1504, 1487, 1461, 1441, 1376, 1368 cm^{-1}; MS (ESI) *m/z* 486.2640 $[M+Na]^+$. Anal. Calcd for $C_{25}H_{41}NO_5Si$: C, 64.76; H, 8.91; N, 3.02. Found: C, 64.42; H, 9.05; N, 2.89.

*6.4.6. (−)-(S)-(E)-Diisopropylcarbamic acid tributylstannyl-[6-(4-triethylsilanyloxy-but-2-enyl)-benzo[1,3]dioxol-5-yl]-methyl ester (**33**)*

Asymmetric stannylation was achieved—according to the protocol used for the synthesis of stannane **23**—using silyl ether **32** (464 mg, 1.00 mL), dissolved in 5 mL of dry diethyl ether, bis(oxazoline) **27** (386 mg, 1.20 mmol), *sec*-butyllithium (0.98 mL of a 1.22 M, 1.20 mmol), and tributyltin chloride (422 mg, 1.30 mmol). Flash chromatography on silica gel (*E*/*P*=1:20) was used for purification. Stannane (−)-(*S*)-(*E*)-**33** (531 mg, 71%) was obtained as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.76 (*E*/*P*=1:1); $[\alpha]_D^{20}$ −7.5 (*c* 1.03, $CHCl_3$), 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (q, ^3J=8.0 Hz, 6H, H_3CCH_2–), 0.81 (t, ^3J=6.9 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 0.93 (t, ^3J=6.9 Hz, 9H, H_3CCH_2–), 1.14–1.44 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.21 (d, ^3J=6.9 Hz, 12H, $(H_3C)_2CH$–), 3.10 (dd, ^2J=16.0 Hz, ^3J=6.9 Hz, 1H, –CH_AH_BCH=CHCH_2O–), 3.23 (ddd, ^2J=16.0 Hz, ^3J=6.4 Hz, ^4J=1.1 Hz, 1H, –CH_AH_BCH=CHCH_2O–), 3.93 (sept, ^3J=6.9 Hz, 2H, H-8), 4.13 (dd, ^3J=5.5 Hz, ^4J=1.3 Hz, 2H, –CH_AH_BCH=CHCH_2O–), 5.60 (tdt, ^3J=15.3, 5.5 Hz, ^4J=1.1 Hz, 1H, –CH_AH_BCH=CHCH$_2O$–), 5.73 (s, 1H, $H_{benzylic}$), 5.70–5.79 (m, 1H, –CH_AH_BCH=CHCH_2O–), 5.87 (s, 2H, –CH_2–), 6.60 (s, 1H, H-5), 6.76 (s, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.5 (H_3CCH_2–), 6.7 (H_3CCH_2–), 10.4 ($H_3CCH_2CH_2CH_2$–), 13.6 ($H_3CCH_2CH_2CH_2$–), 21.0 ($(H_3C)_2$CH–), 27.5 ($H_3CCH_2CH_2CH_2$–), 28.9 (H_3CCH_2–CH_2CH_2–), 35.0 (–CH_AH_BCH=CHCH_2O–), 45.8 ($(H_3C)_2$CH–), 63.5 (–CH_AH_BCH=CH–CH_2O–), 71.7 ($C_{benzylic}$), 100.5 (–CH_2–), 105.5 (C-2), 109.0 (C-5), 126.9 (–CH_AH_B–CH=CHCH_2O–), 128.9 (C-6), 131.3 (–CH_AH_BCH=CH–CH_2O–), 134.8 (C-1), 144.9 (C-3), 146.1 (C-4), 155.4 (NC=O); IR (ATR) 3065, 3018, 2997, 2959, 2936, 2912, 2876, 1692, 1457, 1436, 1368 cm^{-1}; MS (ESI) *m/z* 776.3699 $[M+Na]^+$. Anal. Calcd for $C_{37}H_{67}NO_5SiSn$: C, 59.04; H, 8.97; N, 1.86. Found: C, 58.95; H, 9.09; N, 1.78.

*6.4.7. (−)-(S)-(E)-N,N-Diisopropylcarbamic acid [6-(4-hydroxy-but-2-enyl)-benzo[1,3]dioxol-5-yl]-tributylstannyl-methyl ester (**34**)*

Silyl ether **33** (511 mg, 0.68 mmol) was dissolved in a mixture consisting of 3 mL of THF and 3 mL of water. The solution was cooled to 0 °C and 0.5 mL of trifluoroacetic acid was added dropwise. The reaction mixture was stirred over night at 0 °C. When the reaction was complete (TLC control), the mixture is diluted with 10 mL of TBME and 5 mL of water, warmed to rt, and the phases were separated. The aqueous phase was extracted with TBME (3×10 mL). The combined organic phases were washed with satd $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography on silica gel (*E*/*P*=1:3) afforded (−)-(*S*)-(*E*)-**34** (264 mg, 61%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.33 (*E*/*P*=1:1); $[\alpha]_D^{20}$ −6.9 (*c* 0.51, $CHCl_3$); HPLC: Chiralcel AD-H (4.6×250 mm), H/^{i}PrOH=200:1, 0.3 mL min^{-1}, λ 210 nm, t_R(+) 63.2 min, t_R(−) 77.8 min, 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, ^3J=6.8 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.16–1.48 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.23 (d, ^3J=6.7 Hz, 12H, $(H_3C)_2$CH–), 2.49 (ps-s, 1H, OH), 3.12 (ddd, ^2J=15.8 Hz, ^3J=4.8 Hz, ^4J=1.1 Hz, 1H, –CH_AH_BCH=CHCH_2O–), 3.20 (dd, ^3J=6.8 Hz, ^2J=15.8 Hz, 1H, –CH_AH_BCH=CHCH_2O–), 3.86 (ps-s, 1H, $(H_3C)_2CH$–), 4.05 (ps-s, 1H, $(H_3C)_2CH$–), 4.07 (m, 2H, –CH_AH_BCH=CHCH_2O–), 5.67 (tdt, ^3J=15.4, 6.1 Hz, ^4J=1.1 Hz, 1H, –CH_AH_BCH=CHCH$_2O$–), 5.76 (m, 1H, –CH_AH_BCH=CHCH_2O–), 5.90 (s, 2H, –CH_2–), 6.02 (s, 1H, $H_{benzylic}$), 6.59 (s, 1H, H-5), 6.75 (s, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1 ($H_3CCH_2CH_2CH_2$–), 13.5 ($H_3CCH_2CH_2CH_2$–), 21.1 ($(H_3C)_2$CH–), 27.4 (H_3CCH_2–CH_2CH_2–), 28.7 (H_3CCH_2–CH_2CH_2–), 35.9 (–CH_AH_BCH=CHCH_2O–), 46.0 ($(H_3C)_2$CH–), 63.6 (–CH_AH_BCH=CH–CH_2O–), 70.6 ($C_{benzylic}$), 100.5 (–CH_2–), 105.3 (C-2), 109.7 (C-5), 125.7 (–CH_AH_BCH=CHCH_2O–), 130.6 (C-6), 130.8 (–CH_AH_BCH=CHCH$_2O$–), 135.7 (C-1), 144.8 (C-3), 146.5 (C-4), 155.2 (NC=O); IR (ATR) 3432, 3065, 2956, 2923, 2871, 2854, 1676, 1617, 1504, 1483, 1436, 1376 cm^{-1}; MS (ESI) *m/z* 662.2845 $[M+Na]^+$. Anal. Calcd for $C_{31}H_{53}NO_5Sn$: C, 58.32; H, 8.37; N, 2.19. Found: C, 58.45; H, 8.42; N, 2.02.

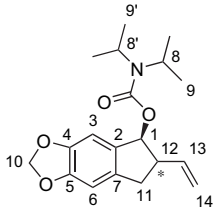
*6.4.8. (−)-(S)-(E)-N,N-Diisopropylcarbamic acid [6-(4-bromo-but-2-enyl)-benzo[1,3]dioxol-5-yl]-tributylstannyl-methyl ester (**35**)*

According to the synthesis of allyl bromide **25**, allyl alcohol **34** (254 mg, 0.40 mmol) was converted into allyl bromide derivative **35** using tetrabromomethane (166 mg, 0.50 mmol) and triphenylphosphine (157 mg, 0.60 mmol). Flash chromatography on silica gel (*E*/*P*=1:15) afforded (−)-(*S*)-(*E*)-**35** (210 mg, 75%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.73 (*E*/*P*=1:1); $[\alpha]_D^{20}$ −12.4 (*c* 0.50, $CHCl_3$), 97% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 (t, ^3J=7.4 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.09–1.62 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.17 (d, ^3J=6.7 Hz, 12H, $(H_3C)_2$CH–), 3.10 (dd, ^2J=15.8 Hz, ^3J=6.7 Hz, 1H, –CH_AH_B–CH=CHCH_2Br), 3.21 (ps-dd, ^2J=15.8 Hz, ^3J=6.3 Hz, 1H, –CH_AH_BCH=CHCH_2Br), 3.88 (ps-s, 2H, $(H_3C)_2CH$–), 3.90 (dd, ^3J=7.5 Hz, ^4J=0.7 Hz, 2H, –CH_AH_BCH=CHCH_2Br), 5.66 (tdt, ^3J=15.0, 7.4 Hz, ^4J=1.3 Hz, 1H, –CH_AH_BCH=CHCH$_2$Br), 5.67 (s, 1H, $H_{benzylic}$), 5.77–5.86 (m, 1H, –CH_AH_BCH=CHCH_2Br), 5.84 (s, 2H, –CH_2–), 6.52 (s, 1H, H-5), 6.7 (s, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.4 ($H_3CCH_2CH_2CH_2$–), 13.6 ($H_3CCH_2CH_2CH_2$–), 21.1 ($(H_3C)_2$CH–), 27.5 (H_3CCH_2–CH_2CH_2–), 28.9 ($H_3CCH_2CH_2CH_2$–), 32.8 (–CH_AH_BCH=CHCH_2Br), 35.0 (–CH_AH_BCH=CHCH_2Br), 46.0 ($(H_3C)_2$CH–), 71.5 ($C_{benzylic}$), 100.6 (–CH_2), 105.8 (C-2), 109.2 (C-5), 125.9 (C-6), 127.9 (–CH_AH_BCH=CHCH$_2$Br), 134.0 (–CH_AH_BCH=CHCH_2Br), 135.0 (C-1), 145.1 (C-3), 146.5 (C-4), 155.4 (NC=O); IR (ATR) 3091, 2957, 2924, 2872, 2853, 2764, 2723, 1678, 1618, 1504, 1482, 1464, 1436, 1376 cm^{-1}; MS (ESI) *m/z* 724.1971 $[M+Na]^+$. Anal. Calcd for $C_{31}H_{52}BrNO_4Sn$: C, 53.09; H, 7.47; N, 2.00 Found: C, 53.37; H, 7.62; N, 1.94.

*6.4.9. N,N-Diisopropylcarbamic acid (6-ethenyl-6,7-dihydro-5H-indeno-[5,6-d][1.3]dioxo-5-yl) ester (**36**)*

According to GPA, CuCN (3.5 mg, 0.04 mmol) was suspended in 4.0 mL of dry toluene and allyl bromide derivative **35** (175 mg, 0.26 mmol) was added. The mixture was stirred for 72 h at 70 °C under sealed tube conditions. Work-up was performed as outlined in GPA. Flash chromatography on silica gel (*E*/*P*=1:6) afforded *trans*-**36** and *cis*-**36** as an inseparable mixture (51 mg, 60%), *trans*-**36**/*cis*-**36**=1.1:1 (^{1}H NMR).

Data for (*S*,*S*)-**36** (*trans*-**36**) and (*S*,*R*)-**36** (*cis*-**36**): R_f 0.70 (*E*/*P*=1:1); t_R 14.15 min (1*S*,2*S*) and (1*S*,2*R*) (HP 5); $[\alpha]_D^{20}$ −21.4 (*c* 0.81, $CHCl_3$), *trans*-**36**/*cis*-**36**=1.1:1; HPLC: CHIRA-GROM 2 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(1*S*,2*S**) 23.3 min, t_R(1*R*,2*S**) 33.0 min, 95% ee; t_R(1*S*,2*R**) 26.6 min, t_R(1*R*,2*R**) 41.8 min, 92% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, ^3J=6.4 Hz, 12H, H-9, H-9′ (1*S*,2*S*)), 1.21 (d, ^3J=6.4 Hz, 12H, H-9, H-9′, (1*S*,2*R*)), 2.67 (dd, ^2J=18.4 Hz, ^3J=10.1 Hz, 1H, H_A-11, (1*S*,2*S*)), 2.81–2.97 (m, 2H, H_B-11 (1*S*,2*R*), H-12 (1*S*,2*S*)), 3.00–3.14 (m, 2H, H_A-11 (1*S*,2*R*), H_B-11 (1*S*,2*S*)), 3.28 (m, 1H, H-12 (1*S*,2*R*)), 3.67 (ps-s, 2H, H-8 (1*S*,2*S*) and (1*S*,2*R*)), 4.18 (ps-s, 1H, H-8′ (1*S*,2*S*)), 4.04 (ps-s, 1H, H-8′ (1*S*,2*R*)), 5.06 (ddd, ^2J=1.9 Hz, ^3J=10.2 Hz, ^4J=1.0 Hz, 1H, H_{cis}-14 (1*S*,2*R*)), 5.07 (ddd, ^2J=1.7 Hz, ^3J=10.4 Hz, 1H, ^4J=0.8 Hz, H_{cis}-14 (1*S*,2*S*)), 5.13 (dd, ^2J=1.9 Hz, ^3J=17.2 Hz, 1H, H_{trans}-14 (1*S*,2*R*)), 5.14 (dd, ^2J=1.7 Hz, ^3J=17.2 Hz, 1H, H_{trans}-14 (1*S*,2*S*)), 5.84–5.98 (m, 7H, H-1, H-10, H-13 (1*S*,2*S*), H-10, H-13 (1*S*,2*R*)), 6.04 (d, ^3J=6.5 Hz, 1H, H-1 (1*S*,2*R*)), 6.66 (s, 1H, H-3 (1*S*,2*S*)), 6.69 (s, 1H, H-3 (1*S*,2*R*)), 6.82 (s, 1H, H-6 (1*S*,2*S*)), 6.91 (s, 1H, H-6 (1*S*,2*R*)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (C-9 (1*S*,2*R*)), 21.6 (C-9 (1*S*,2*S*)), 35.7 (C-11 (1*S*,2*S*)), 35.9 (C-11 (1*S*,2*R*)), 45.3 (C-8, C-8′ (1*S*,2*R*)), 46.3 (C-8, C-8′ (1*S*,2*S*)), 48.6 (C-12 (1*S*,2*R*)), 51.3 (C-12 (1*S*,2*S*)), 79.1 (C-1 (1*S*,2*R*)), 81.9 (C-1 (1*S*,2*S*)), 101.4 (C-10 (1*S*,2*S*) and (1*S*,2*R*)), 104.8(6) (C-3, (1*S*,2*S**)), 104.9(1) (C-3, (1*S*,2*R**)), 105.6 (C-6 (1*S*,2*S*)), 106.1 (C-6 (1*S*,2*R*)), 115.5 (C-14 (1*S*,2*S*)), 116.1 (C-14 (1*S*,2*R*)), 134.4 (C-7, (1*S*,2*S**)), 134.5 (C-7, (1*S*,2*R**)), 135.4 (C-13 (1*S*,2*R*)), 136.6 (C-13 (1*S*,2*S*)), 137.2 (C-2 (1*S*,2*R**)), 138.9 (C-2 (1*S*,2*S**)), 146.5 (C-4 (1*S*,2*S**)), 146.7 (C-4 (1*S*,2*R**)), 148.1 (C-5 (1*S*,2*S**)), 148.3 (C-5 (1*S*,2*R**)), 155.3 (NC=O (1*S*,2*S*)), 155.8 (NC=O (1*S*,2*R*)); IR (ATR) 3078, 2970, 2934, 2880, 2852, 2771, 1682, 1644, 1502, 1474, 1436, 1368 cm^{-1}; MS (ESI) *m*/*z* 354.1678 [M+Na]$^+$. Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; N, 4.23. Found: C, 68.74; H, 7.43; N, 4.05.



6.5. Synthesis of tetralines 42

6.5.1. (*E*)-(Penta-2,4-dienyloxy)-triethylsilane (**37**)

Lithium aluminum hydride (397 mg, 10.00 mmol) was suspended in 20 mL of dry diethyl ether and cooled to −15 °C. Penta-2,4-dienoic acid methyl ester (561 mg, 5.00 mmol) was added dropwise via syringe. The reaction mixture was stirred for 2 h at −15 °C. Ice-water of 5 mL was carefully added. When gassing has ceased, sulfuric acid (10%) was added carefully and dropwise until the mixture became clear. The phases were separated and the aqueous one was extracted with diethyl ether (3×20 mL), dried over $MgSO_4$, and carefully concentrated in vacuo (p≥930 mbar) to obtain the crude allyl alcohol.[43]

The crude alcohol was directly dissolved again in 30 mL of THF and the solution was cooled to 0 °C. Triethylamine (1.45 g, 12.5 mmol) and a catalytic amount of DMAP were added and the mixture was stirred until it became clear. Then, triethylsilyl chloride (791 mg, 5.25 mmol) was injected portion wise. The reaction mixture was stirred for 12 h and slowly warmed to rt. Work-up and rough purification by flash chromatography on silica gel (*E*/*P*=1:40) afforded unsaturated silane **37** (942 mg) as colorless, volatile liquid after careful concentration in vacuo (p≥700 mbar), *E*/*Z*=95:5 (^{1}H NMR). Data for (*E*)-**37**: R_f 0.75 (*E*/*P*=1:1); t_R 9.2 min (HP 5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.62 (q, ^3J=7.9 Hz, 6H, H_3CCH_2–), 0.96 (t, ^3J=7.9 Hz, 9H, H_3CCH_2–), 4.21 (dd, ^3J=5.3 Hz, ^4J=1.4 Hz, 2H, H-1), 5.04 (dd, ^2J=2.3 Hz, ^3J=9.8 Hz, 1H, H_{trans}-5), 5.17 (dd, ^2J=2.3 Hz, ^3J=16.2 Hz, 1H, H_{cis}-5), 5.78 (dt, ^3J=5.3, 14.9 Hz, 1H, H-2), 6.24 (ddt, ^3J=14.5, 14.9 Hz, ^4J=1.4 Hz, 1H, H-3), 6.27–6.41 (m, 1H, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.2 (H_3CCH_2–), 6.4 (H_3CCH_2–), 63.0 (C-1), 116.7 (C-5), 130.7 (C-2), 133.2 (C-3), 136.6 (C-4); IR (ATR) 3095, 3065, 2955, 2913, 2877, 1726, 1605, 1504, 1459, 1415, 1374 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{22}OSi$: *m*/*z* 221.1332 [M+Na]$^+$, 419.2772 [2M+Na]$^+$, found: *m*/*z* 221.1318 [M+Na]$^+$, 419.2769 [2M+Na]$^+$.

6.5.2. (*E*)-*N*,*N*-Diisopropylcarbamic acid 2-(5-triethylsilanyloxy-pent-3-enyl)-benzyl ester (**38**)

Firstly, unsaturated silyl ether (*E*)-**37** was dissolved in 5.0 mL of dry THF and the solution was cooled to 0 °C. A solution of 9-borabicyclo[3.3.1]nonane (10.00 mL of a 0.5 M solution in THF, 5.00 mmol) was injected slowly and the reaction mixture was kept stirring for 6 h and finally warmed to rt. The resulting solution was directly used in the following coupling reaction.

Potassium phosphate (955 mg, 4.50 mmol) was weighted into a Schlenk tube. *ortho*-Iodo-substituted benzyl carbamate **18** (1.62 g, 4.50 mmol) and $Pd(PPh_3)_4$ (156 mg, 0.14 mmol) were added. The solids were dissolved in 10 mL of dry DMF and the borane-containing THF-solution was added by transfer cannula. The reaction mixture was heated to 60 °C and stirred for 32 h (sealed tube). For work-up, the reaction mixture was cooled to rt, diluted with 10 mL of TBME and 10 mL of water. The phases were separated and the aqueous one was extracted with TBME (3×20 mL). The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography on silica gel afforded silylated allyl alcohol (*E*)-**38** (1.62 g, 83%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.74 (*E*/*P*=1:1); t_R 23.3 min (HP 5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60 (q, ^3J=7.8 Hz, 6H, H_3CCH_2–), 0.95 (t, ^3J=7.8 Hz, 9H, H_3CCH_2–), 1.19 (ps-s, 12H, $(H_3C)_2CH$–), 2.33 (dtd, ^3J=8.2, 6.7 Hz, ^4J=1.1 Hz, 2H, –CH_2CH_2CH=$CHCH_2O$–), 2.71–2.78 (m, 2H, –CH_2CH_2–CH=$CHCH_2O$–), 3.91 (ps-s, 2H, $(H_3C)_2CH$–), 4.10 (dd, ^3J=5.4 Hz, ^4J=1.2 Hz, 2H, –CH_2CH_2CH=$CHCH_2O$–), 5.15 (s, 2H, $H_{benzylic}$), 5.59 (tdt, ^3J=15.3, 5.4 Hz, ^4J=1.1 Hz, 1H, –CH_2CH_2CH=$CHCH_2O$–), 5.71 (tdt, ^3J=15.3, 6.7 Hz, ^4J=1.2 Hz, 1H, –CH_2CH_2CH=$CHCH_2O$–), 7.15–7.31 (m, 3H, H-3, H-4, H-5), 7.32–7.37 (m, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3 (H_3CCH_2–), 6.4 (H_3CCH_2–), 20.3 ($(H_3C)_2CH$–), 31.9 (–CH_2CH_2CH=$CHCH_2O$–), 33.3 (–CH_2CH_2CH=$CHCH_2O$–), 45.6 ($(H_3C)_2CH$–), 63.3 (–CH_2CH_2CH=$CHCH_2O$–), 64.0 ($C_{benzylic}$), 126.1 (C-5), 128.1 (C-6), 129.3 (C-4), 129.4 (C-3), 129.9 (–CH_2CH_2CH=$CHCH_2O$–), 130.4 (–CH_2CH_2CH=CH–CH_2O–), 134.5 (C-2), 140.4 (C-1), 155.3 (NC=O); IR (ATR) 3024, 2960, 2933, 2914, 2876, 2855, 1693, 1452, 1439, 1377, 1368 cm^{-1}; MS (ESI) *m*/*z* 456.2908 [M+Na]$^+$. Anal. Calcd for $C_{25}H_{43}NO_3Si$: C, 69.23; H, 9.99; N, 3.23. Found: C, 68.88; H, 10.13; N, 3.19.

6.5.3. (−)-(*S*)-(*E*)-*N*,*N*-Diisopropylcarbamic acid tributylstannyl-[2-(5-triethylsilanyloxy-pent-3-enyl)-phenyl]-methyl ester (**39**)

Asymmetric stannylation was achieved—according to the protocol used for the synthesis of stannane **23**—using silyl ether **38** (434 mg, 1.00 mmol), dissolved in 5 mL of dry diethyl ether, bis(oxazoline) **27** (386 mg, 1.20 mmol), *sec*-butyllithium (0.98 mL of 1.22 M, 1.20 mmol), and tributyltin chloride (424 mg, 1.30 mmol). Flash chromatography on silica gel (*E*/*P*=1:20) afforded stannane (−)-(*S*)-(*E*)-**39** (480 mg, 66%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.75 (*E*/*P*=1:1); $[\alpha]_D^{20}$ −27.6 (*c* 1.07, $CHCl_3$), 72% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (q, ^3J=8.0 Hz, 6H, H_3CCH_2–), 0.81 (t, ^3J=7.2 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 0.96 (t, ^3J=8.0 Hz, 9H, H_3CCH_2–), 1.15–1.41 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.23 (d, ^3J=7.0 Hz, 12H, $(H_3C)_2CH$–), 2.22–2.34 (m, 1H, –$CH_AH_BCH_AH_BCH$=$CHCH_2O$–), 2.34–2.45 (m, 1H, –$CH_AH_BCH_AH_BCH$=$CHCH_2O$–), 2.46–2.53 (m, 1H, –$CH_AH_BCH_AH_BCH$=$CHCH_2O$–), 2.53–2.63 (m, 1H, –CH_AH_B-CH_AH_BCH=$CHCH_2O$–), 3.97 (sept, ^3J=7.0 Hz, 2H, H-8, $(H_3C)_2CH$–), 4.11 (dd, ^3J=5.4 Hz, ^4J=1.2 Hz, 2H, –$CH_AH_BCH_AH_BCH$=$CHCH_2O$–),

5.63 (dtd, ^3J=15.1, 5.4 Hz, ^4J=1.2 Hz, 1H, –$CH_AH_BCH_AH_BCH$=C*H*–CH_2O–), 5.74 (ps-ddt, ^3J=15.1, 6.4 Hz, ^4J=1.2 Hz, 1H, –$CH_AH_BCH_AH_B$–C*H*=$CHCH_2O$–), 5.84 (s, 1H, $H_{benzylic}$), 7.02 (ddd, ^3J=^3J=7.3 Hz, ^4J=1.3 Hz, 1H, H-5), 7.09 (dd, ^3J=7.8 Hz, ^4J=1.3 Hz, 1H, H-3), 7.15 (ddd, ^3J=7.8, 7.3 Hz, ^4J=1.4 Hz, 1H, H-4), 7.26 (ps-d, ^3J=7.3 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.5 (H_3CCH_2–), 6.7 (H_3CCH_2–), 10.5 ($H_3CCH_2CH_2CH_2$–), 13.6 ($H_3CCH_2CH_2CH_2$–), 21.0 ((H_3C)$_2$CH–), 27.5 ($H_3CCH_2CH_2CH_2$–), 28.9 (H_3CCH_2–CH_2CH_2–), 32.4 (–*C*H_AH_B–CH_AH_BCH=CH–CH_2O–), 32.6 (–$CH_AH_BCH_AH_BCH$=$CHCH_2O$–), 45.9 ((H_3C)$_2$*C*H–), 63.6 (–$CH_AH_BCH_AH_BCH$=*C*HCH_2O–), 71.8 ($C_{benzylic}$), 124.7 (C-5), 124.8 (C-6), 126.2 (C-4), 128.6 (C-3), 129.7 (–CH_AH_B–*C*H_AH_BCH=$CHCH_2O$–), 130.8 (–$CH_AH_BCH_AH_B$–CH=*C*HCH_2O–), 134.9 (C-2), 141.2 (C-1), 155.5 (NC=O); IR (ATR) 3062, 2957, 2931, 2875, 2854, 1680, 1601, 1478, 1462, 1440, 1433, 1377, 1368 cm^{-1}; MS (ESI) *m*/*z* 746.3978 [M+Na]$^+$. Anal. Calcd for $C_{37}H_{69}NO_3SiSn$: C, 61.49; H, 9.62; N, 1.94. Found: C, 61.46; H, 9.76; N, 1.91.

6.5.4. (–)-(S)-(E)-N,N-Diisopropylcarbamic acid [2-(5-hydroxy-pent-3-enyl)-phenyl]-tributylstannyl-methyl ester (**40**)

According to the synthesis of allyl alcohol **34**, desilylation was accomplished by dissolving silyl ether **39** (325 mg, 0.45 mmol) in 3 mL THF and 3 mL water and adding 0.5 mL trifluoroacetic acid. Work-up and purification by flash chromatography on silica gel (*E*/*P*=1:8) afforded allyl alcohol derivative (–)-(*S*)-(*E*)-**40** (158 mg, 65%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.27 (*E*/*P*=1:1); $[\alpha]_D^{20}$ –46.1 (*c* 0.95, $CHCl_3$), 72% ee; HPLC: Chiralcel AD-H (4.6×250 mm), H/^{i}PrOH=200:1, 0.3 mL min^{-1}, λ 210 nm, t_R(+) 43.3 min, t_R(–) 46.1 min, 72% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, ^3J=7.5 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.10–1.39 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.18 (d, ^3J=6.4 Hz, 12H, (H_3C)$_2$CH–), 2.19 (ps-s, 1H, O*H*), 2.26–2.40 (m, 2H, –$CH_AH_BCH_AH_B$–CH=$CHCH_2O$–), 2.47–2.54 (m, 1H, –$CH_AH_BCH_AH_B$–CH=$CHCH_2O$–), 3.95 (sept, ^3J=6.4 Hz, 2H, (H_3C)$_2$C*H*–), 4.00 (dd, ^3J=7.7 Hz, ^4J=3.3 Hz, 2H, –$CH_AH_BCH_AH_BCH$=CHCH_2O–), 5.63 (m, 1H, –$CH_AH_BCH_AH_BCH$=C*H*CH_2O–), 5.67 (m, 1H, –$CH_AH_BCH_AH_BCH$=CH–CH_2O–), 6.00 (s, 1H, $H_{benzylic}$), 6.99 (ddd, ^3J=^3J=7.3 Hz, ^4J=1.3 Hz, 1H, H-5), 7.05 (dd, ^3J=7.8 Hz, ^4J=1.3 Hz, 1H, H-3), 7.12 (ddd, ^3J=7.8, 7.3 Hz, ^4J=1.6 Hz, 1H, H-4), 7.20 (ps-d, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1 (H_3C–$CH_2CH_2CH_2$–), 13.3 ($H_3CCH_2CH_2CH_2$–), 20.8 ((H_3C)$_2$CH–), 27.2 ($H_3CCH_2CH_2CH_2$–), 28.5 ($H_3CCH_2CH_2$–CH_2–), 32.1 (–*C*H_AH_B–CH_AH_BCH=$CHCH_2O$–), 33.0 (–$CH_AH_BCH_AH_B$–CH=$CHCH_2O$–), 45.7 ((H_3C)$_2$*C*H–), 63.1 (–CH_AH_B–CH_AH_BCH=$CHCH_2O$–), 71.5 ($C_{benzylic}$), 124.3 (C-5), 124.7 (C-6), 126.2 (C-4), 128.9 (C-3), 130.2 (–CH_AH_B–CH_AH_BCH=$CHCH_2O$–), 131.2 (–$CH_AH_BCH_AH_BCH$=*C*HCH_2O–), 134.6 (C-2), 141.5 (C-1), 155.4 (NC=O); IR (ATR) 3448, 3065, 2997, 2956, 2928, 2854, 1675, 1601, 1543, 1477, 1463, 1434, 1377, 1369 cm^{-1}; MS (ESI) *m*/*z* 632.3108 [M+Na]$^+$. Anal. Calcd for $C_{31}H_{55}NO_3Sn$: C, 61.19; H, 9.11; N, 2.30. Found: C, 61.42; H, 9.28; N, 2.19.

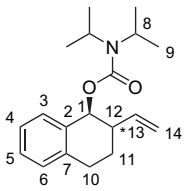
6.5.5. (–)-(S)-(E)-N,N-Diisopropylcarbamic acid [2-(5-bromo-pent-3-enyl)-phenyl]-tributylstannyl-methyl ester (**41**)

According to the synthesis of allyl bromide **35**, allyl alcohol **40** (122 mg, 0.20 mmol) was converted into allyl bromide derivative **41** using tetrabromomethane (83 mg, 0.25 mmol) and triphenylphosphine (79 mg, 0.30 mmol). Flash chromatography on silica gel (*E*/*P*=1:15) afforded (–)-(*S*)-(*E*)-**41** (130 mg, 97%) as colorless liquid, *E*/*Z*≥98:2 (^{1}H NMR). R_f 0.76 (*E*/*P*=1:1); $[\alpha]_D^{20}$ –3.9 (*c* 0.49, $CHCl_3$), 72% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, ^3J=7.2 Hz, 9H, $H_3CCH_2CH_2CH_2$–), 1.13–1.43 (m, 18H, $H_3CCH_2CH_2CH_2$–), 1.24 (d, ^3J=6.9 Hz, 12H, (H_3C)$_2$CH–), 2.23–2.43 (m, 2H, –$CH_AH_BCH_AH_BCH$=$CHCH_2Br$), 2.45–2.60 (m, 2H, –$CH_AH_BCH_AH_BCH$=$CHCH_2Br$), 3.94 (dd, ^3J=7.5 Hz, ^4J=0.7 Hz, 2H, –$CH_AH_BCH_AH_BCH$=$CHCH_2Br$), 3.97 (ps-s, 2H, (H_3C)$_2$C*H*–), 5.75 (tdt, ^3J=7.5, 15.3 Hz, ^4J=1.2 Hz, 1H, –$CH_AH_BCH_AH_BCH$=C*H*CH_2Br), 5.84 (s, 1H, $H_{benzylic}$), 5.85 (dt, ^3J=15.3, 6.6 Hz, 1H, –CH_AH_B–CH_AH_BCH=CH–CH_2Br), 7.03 (ddd, ^3J=7.2, 7.0 Hz, ^4J=1.2 Hz, 1H, H-5), 7.07 (dd, ^3J=7.5 Hz, ^4J=1.2 Hz, 1H, H-3), 7.16 (ddd, ^3J=7.5, 7.0 Hz, ^4J=1.7 Hz, 1H, H-4), 7.27 (ps-d, ^3J=7.2 Hz, 1H, H-6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.4 (H_3CCH_2–CH_2CH_2–), 13.6 ($H_3CCH_2CH_2CH_2$–), 20.9 ((H_3C)$_2$CH–), 27.5 (H_3CCH_2–CH_2CH_2–), 28.8 (H_3CCH_2–CH_2CH_2–), 31.9 (–*C*$H_AH_BCH_AH_BCH$=$CHCH_2Br$), 32.3 (–$CH_AH_BCH_AH_B$–C*H*=$CHCH_2Br$), 33.2 (–$CH_AH_BCH_AH_B$–C*H*=$CHCH_2Br$), 45.7 ((H_3C)$_2$CH–), 71.6 ($C_{benzylic}$), 124.8 (C-5), 126.3 (C-6), 126.9 (C-4), 128.5 (C-3), 134.3 (–$CH_AH_BCH_AH_B$–*C*H=$CHCH_2Br$), 135.5 (–$CH_AH_BCH_AH_BCH$=*C*HCH_2Br), 141.2 (C-2), 141.3 (C-1), 155.2 (NC=O); IR (ATR) 3064, 2957, 2924, 2871, 2854, 2759, 2723, 1679, 1631, 1601, 1548, 1464, 1433, 1378, 1369 cm^{-1}; MS (ESI) *m*/*z* 694.2244 [M+Na]$^+$. Anal. Calcd for $C_{31}H_{54}BrNO_2Sn$: C, 55.46; H, 8.11; N, 2.09. Found: C, 55.38; H, 8.19; N, 1.96.

6.5.6. N,N-Diisopropylcarbamic acid 2-ethenyl-1,2,3,4-tetrahydro-naphthalen-1-yl ester (**42**)

According to GPA, CuCN (2.0 mg, 0.02 mmol) was suspended in 2.0 mL of dry toluene and allyl bromide derivative **41** (100 mg, 0.15 mmol) was added. The mixture was stirred for 72 h at 70 °C under sealed tube conditions. Work-up was performed as outlined in GPA. Flash chromatography on silica gel (*E*/*P*=1:6) afforded *trans*-**42** and *cis*-**42** as an inseparable mixture (30 mg, 66%), *trans*-**42**/*cis*-**42**=1.5:1 (^{1}H NMR).

Data for *trans*-**42** ((1*S*,2*S*)-**42**) and *cis*-**42** ((1*S*,2*R*)-**42**): R_f 0.67 (*E*/*P*=1:1); t_R 17.6 min (1*S*,2*R*), 17.7 min (1*S*,2*S*) (HP 5); $[\alpha]_D^{20}$ –38.5 (*c* 0.81, $CHCl_3$) *trans*-**42**/*cis*-**42**=1.5:1; HPLC: CHIRA-GROM 1 (2×250 mm), H/^{i}PrOH=1000:1, 0.3 mL min^{-1}, λ 210 nm, t_R(1*S*,2*R*) 15.7 min, t_R(1*R*,2*R*) 21.8 min, 70% ee; t_R(1*S*,2*S*) 25.1 min, t_R(1*R*,2*S*) 39.7 min, 68% ee; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (br d, ^3J=6.8 Hz, 12H, H-9 (1*S*,2*S*)), 1.16 (br d, ^3J=6.8 Hz, 12H, H-9 (1*S*,2*R*)), 1.75 (ddt, ^2J=18.4 Hz, ^3J=^3J=6.2 Hz, 1H, H_A-11 (1*S*,2*R*)), 1.88–2.06 (m, 3H, H_B-11 (1*S*,2*R*), H_A-11, H_B-11, (1*S*,2*S*)), 2.52–2.68 (m, 2H, H-12 (1*S*,2*S*) and (1*S*,2*R*)), 2.72–2.99 (m, 4H, H_A-10, H_B-10 (1*S*,2*S*) and (1*S*,2*R*)), 3.67 (ps-s, 2H, H-8 (1*S*,2*S*)), 4.04 (ps-s, 2H, H-8 (1*S*,2*R*)), 4.98 (ddd, ^2J=1.7 Hz, ^3J=10.3 Hz, ^4J=1.0 Hz, 1H, H_{cis}-14 (1*S*,2*R*)), 5.01–5.08 (m, 2H, H_{trans}-14 (1*S*,2*S*) and (1*S*,2*R*)), 5.10 (ddd, ^2J=1.6 Hz, ^3J=11.4, 1.5 Hz, 1H, H_{cis}-14 (1*S*,2*S*)), 5.76 (ddd, ^3J=7.7, 17.3, 10.3 Hz, 1H, H-13 (1*S*,2*R*)), 5.86 (br d, ^3J=8.2 Hz, 1H, H-1 (1*S*,2*R*)), 5.83–5.92 (m, 1H, H-13 (1*S*,2*S*)), 6.02–6.07 (m, 1H, H-1 (1*S*,2*S*)), 6.99–7.44 (m, 8H, H-ph (1*S*,2*S*) and (1*S*,2*R*)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (C-9 (1*S*,2*R*)), 21.5 (C-9 (1*S*,2*S*)), 23.7 (C-10 (1*S*,2*R*)), 26.7 (C-10 (1*S*,2*S*)), 27.5 (C-11 (1*S*,2*S*)), 28.0 (C-11 (1*S*,2*R*)), 42.4 (C-12 (1*S*,2*R*)), 44.5 (C-12 (1*S*,2*S*)), 45.4 (C-8 (1*S*,2*R*)), 46.3 (C-8 (1*S*,2*S*)), 71.5 (C-1 (1*S*,2*R*)), 73.6 (C-1 (1*S*,2*S*)), 115.4 (C-14 (1*S*,2*R*)), 115.7 (C-14 (1*S*,2*S*)), 125.9(1), 129.9(4), 127.3, 127.8, 128.4, 128.5, 128.7, 129.9 (C-3 to C-6 (1*S*,2*S*) and (1*S*,2*R*)), 135.5 (C-7 (1*S*,2*R*)), 135.7 (C-7 (1*S*,2*S*)), 136.8 (C-2 (1*S*,2*R*)), 136.9 (C-2 (1*S*,2*S*)), 138.8 (C-13 (1*S*,2*R*)), 139.2 (C-13 (1*S*,2*S*)), 155.2 (NC=O (1*S*,2*R*)), 155.6 (NC=O (1*S*,2*S*)); IR (ATR) 3076, 2997, 2969, 2933, 2873, 1683, 1643, 1492, 1476, 1432, 1368 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{27}NO_2$: *m*/*z* 324.1934 [M+Na]$^+$, found: *m*/*z* 324.1939 [M+Na]$^+$.



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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.06.092.

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